Geometric and electronic structure of a C₆₀ monolayer on Ag(100)

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Using scanning tunneling microscopy and spectroscopy and first principles calculations, we have systematically studied the morphological and electronic structures of a C₆₀ monolayer on Ag(100). Our results reveal that the bright-dim contrast has a definite geometric origin and there are two types of dim C₆₀ molecules, one a monomer and the other a dimer. With distinctive electronic properties and distinctive charge transfers in the differently adsorbed C₆₀ molecules, this C₆₀ monolayer is highly inhomogeneous and aperiodic.

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INTRODUCTION

The adsorption of C₆₀ monolayers on metal and semiconductor surfaces has been extensively studied in the past.^{1–19} Among these adsorption systems, C₆₀ on Ag(100) has attracted particular attention. The widely quoted charge transfer of ~ 2.7 electrons from the metal substrate to each C₆₀ molecule as observed in an electron energy loss spectroscopy (EELS) study⁸ has stimulated great interest in the possible two-dimensional superconducting states of this system.^{10–15,20} Analogous to the bulk fulleride superconductors A₃C₆₀ (A=K,Cs), a charge transfer of three electrons to each C₆₀ molecule would lead to half-filling of the lowest-unoccupied-molecular-orbital (LUMO) band and thus would meet the essential requirement for a superconductive state.²¹ The gap opening near the Fermi level observed through photoemission spectroscopy (PES) at temperatures as high as 250 K,¹⁰ although seriously challenged,²⁰ was speculated to be evidence of the superconducting state of this system.¹⁰

Scanning tunneling microscopy (STM) has been used to investigate this system intensively on its morphology^{6,12–14} but rarely on its electronic property.¹² In well-annealed C₆₀ monolayers, a bright-dim (BD) contrast was observed in STM images, indicating that there are at least two different kinds of C₆₀ adsorption. However, whether the origin of this contrast is from the electronic effect,⁶ the molecular orientation,^{11,15} or the geometric effect upon the Ag substrate reconstruction^{12–14} remains controversial up to today. Combined with careful examinations of low energy electron diffraction patterns, Pai *et al.* identified a completely different overlayer structure¹³ than the $c(6 \times 4)$ structure reported in the earlier studies.^{8,10} They found that C₆₀/Ag(100) forms an incommensurate and aperiodic (111) close-packed phase with only short-range order,¹⁴ in addition to a geometrical origin of BD contrast. However, only the molecular orientation difference instead of the geometric origin is appreciated in a more recent study with photoemission spectroscopy.¹⁵ The early report of a charge transfer of $2.7e/C_{60}$ from Ag(100) (Ref. 8) has been challenged by a later PES study that reports $\sim 1.7e/C_{60}$ for a monolayer⁹ and by a calculation

that reports an even lower value for an *isolated* C₆₀ molecule.¹⁶ To resolve the above issues, in this paper, we combine our STM studies with first principles calculations and explicitly show that the BD contrast in C₆₀/Ag(100) is mainly a geometric effect. Most importantly, we demonstrate that there are two kinds of dim (D) C₆₀ molecules: one as monomer and the other as dimer. The electronic properties and the charge transfers are found drastically different in differently adsorbed C₆₀ molecules and the resulting monolayer is highly aperiodic.

METHODS

Experiments. We performed our experiments at 77 K in an Omicron low temperature STM system with a base pressure $< 1 \times 10^{-10}$ Torr. The local differential conductance (dI/dV) curves were obtained numerically from the measured I - V curves. A clean single crystal Ag(100) substrate ($< 0.1^\circ$ miscut) was obtained by repetitive cycles of 1 keV Ar⁺ sputtering and high temperature annealing at ~ 750 K. The C₆₀ molecules were deposited at a rate of ~ 0.1 ML/min at a substrate temperature of 600 K for 30 min, followed by additional 30 min of annealing at 600 K to remove any C₆₀ multilayers.^{9,10,12} The final surface was mostly covered by a full C₆₀ monolayer, with occasionally a little bare Ag(100) area left in a densely packed step region for checking the electronic states of the STM tips. As shown by Refs. 13 and 14, samples prepared by the above procedure have reached thermal equilibrium state in terms of inducing substrate reconstruction.

Simulations. To establish the links between our observations and the adsorption structures and charge states of different types of adsorbed C₆₀ molecules, we performed first-principles density functional theory calculations.^{22,23} A repeated-slab geometry that consisted of four layers of Ag, one layer of C₆₀, and a 10 Å vacuum spacer was used. Depending on the chosen configuration, each Ag layer consists of 24 to 35 Ag atoms and the C₆₀ layer consists of one to three molecules. Our calculations used the generalized gradient approximation with the Perdew, Burke, and Ernzerhof

FIG. 1. (Color online) (a)–(d) 10 nm $\times$ 10 nm STM images of $C_{60}/Ag(001)$ taken at 1 nA and various biases. The bright C_{60} and the dim C_{60} with and without a close dim neighbor are labeled as B, DM, and DD, respectively, in (a). Differently oriented B and DD molecules are highlighted in (b). The crystallographic direction $[110]$ is labeled in (b) by a white line, and the “pseudo- $c(6 \times 4)$ ” unit cell is labeled in (a) by a dashed white rectangle. (e) The BD contrast as a function of sample bias. (f) An example of the line profiles at two different biases of -0.5 and $+0.5$ V.

exchange-correlation functional²⁴ and the projector augmented-wave^{25,26} with a plane wave basis. The basis set cutoff was 400 eV. During the structural optimization, we fixed the atoms of the lower Ag layers in their bulk positions and only allowed the C_{60} molecules and the top two layers of Ag atoms to fully relax until the forces were less than 50 meV/Å. To compare the results with experimental data, we present the partial density of states of the whole C_{60} molecule (C_{60} -DOS) and that of the topmost six C atoms (6C-DOS) within a circle of 4.4 Å, comparable with the finite tip size used in measuring the dI/dV spectra. While the experiments clearly showed no periodic structures for the C_{60} monolayer on Ag(100), in the simulations, we will have to use some kind of periodic structures that have a close similarity in spatial positions to the observations as detailed in the results section. All the calculations were performed on a super computer with 512 CPU nodes and some runs of the structural optimization have taken more than 20 days.

RESULTS AND DISCUSSION

In Fig. 1, we show a number of STM images of the C_{60} monolayer on Ag(001) taken at various bias voltages over the same area with a sharp tip. A number of features are noted. (i) There is a clear BD contrast among C_{60} molecules at all biases. The number of bright and dim molecules as counted in an image with 540 molecules has a ratio of 37:63, comparable with results in Ref. 12. (ii) Among the dim C_{60} molecules, there are two distinct types: one with a close dim neighbor separated by ~ 9.4 Å (labeled DD), forming a tetramer together with two bright neighbor C_{60} molecules (labeled by black lines), and the other with no close dim neighbor (labeled DM). The ratio of DD to DM molecules is 53:47. (iii) The internal C_{60} molecular structures are clearly resolved at negative biases but only faintly noticeable at positive biases. As shown in Fig. 1(b), while the DD molecules show asymmetric nodal structures, the bright mol-

FIG. 2. (Color online) (a) A $11.8 \text{ nm} \times 16.5 \text{ nm}$ STM image with chronologically labeled positions at which the I - V curves shown in (b) were taken. (c) The averaged dI/dV curves for B, DM, and DD molecules, together with that of bare Ag. The vertical arrows are the peak positions from Gaussian fits.

ecules show three lobes with two nonequivalent but nearly opposite orientations. This observation is consistent with that in Refs. 13 and 14 but somewhat different from that in Ref. 12. In the latter the clear internal features were reported only at +2 V but not at negative bias. (iv) Through a careful examination of all the STM images, we found that, either with or without the internal C_{60} structure resolved, there is a bias-dependent BD contrast in all samples even when different tips are used [Fig. 1(e)]. The height difference is $\sim 1.1 \text{ \AA}$ at all negative biases but increases to $\sim 1.6 \text{ \AA}$ at higher positive biases.

To identify the adsorption structures of the different types of C_{60} molecules, we used molecular-resolved scanning tunneling spectroscopy (STS) measurements. In order to avoid the position dependence of I - V spectra within the C_{60} molecules,^{12,16} we used a blunt tip that was sharp enough to resolve individual C_{60} molecules but blunt enough to average out the local density of states (DOS) without revealing the internal molecular structures [Fig. 2(a)], indicating a tip apex with comparable but smaller size than that of a C_{60} molecule. In Fig. 2(b), a series of I - V spectra were taken following an order as indicated in Fig. 2(a) which is random among the three types of C_{60} molecules. These I - V spectra surprisingly fall into three groups: those on the B molecules, those on the DM molecules, and those on the DD molecules. The same behaviors were routinely reproduced on different samples and with different tips. To assure the cleanness of the tips, we checked the tip on the bare Ag regions before and after the C_{60} monolayer measurements. In Fig. 2(c), the averaged differential conductance dI/dV curves for the three types of C_{60} molecules together with that for bare Ag are plotted. Clearly, there are three main features for these molecules: first, a shoulder below -1.5 eV , corresponding to the highest occupied molecular orbital (HOMO), appears for all the molecules with only a small difference in the peak intensities; second, the LUMO+1 states around $+1.5 \text{ eV}$ for DM and DD, on the other hand, are very broad and show a shift towards the Fermi level from that of the B molecules; third, the major difference appears in the LUMO states. For B

molecules, the LUMO shows a strong peak at $\sim 0.53 \text{ eV}$ and a shoulder at $\sim 0.23 \text{ eV}$. For DM molecules, the strength of the LUMO peak at 0.53 eV is much reduced and becomes comparable to that at 0.15 eV . For the DD molecules, the spectrum in the range of -1.2 to $+1.0 \text{ eV}$ is practically flat. Our observations of B and DM C_{60} molecules are consistent with those observed on Al(111) (Ref. 3) and those observed earlier on this surface.¹² However, the dI/dV spectrum on DD molecules was observed quite differently from those on B and DM molecules. The electronic nonequivalency of the three types of C_{60} molecules indicates that this monolayer is highly aperiodic aside from the overall close packing.¹⁴

Origin of the bright-dim contrast. Several mechanisms have been proposed to explain the BD contrast, including electronic effects,⁶ molecular orientations,^{11,15} and geometric effects upon the Ag substrate reconstruction.^{13,14} The dI/dV spectra shown in Fig. 2(c) indicate that the B and D molecules have practically the same electronic structure below the Fermi level. It is thus impossible to attribute the large BD contrast ($\sim 1.1 \text{ \AA}$) at negative biases to electronic effects. The larger height difference ($\sim 1.6 \text{ \AA}$) between the B and D molecules at positive biases [Fig. 1(e)] indicates that the difference in the LUMO electronic states indeed contributes to the BD contrast at positive biases.

As shown in Fig. 3, our calculation results from differently oriented C_{60} molecules adsorbed in a $c(6 \times 4)$ unit cell (with spatial positions close to the STM images) on a perfect Ag(100) surface indicate that, either with the 5-6 bond (the bond between a pentagon and a hexagon) facing up, or with the 6-6 bond (the bond between two hexagons) facing up, or with an edge atom facing up (data not shown), or a combination of them,¹⁵ both C_{60} -DOS and 6C-DOS, although exhibiting some difference for the LOMO, LUMO, and LUMO+1 bands, do not show any agreement with experimental observations of the three types of dramatically different dI/dV curves [Fig. 2(c)]. The reason for considering C_{60} molecules with either 5-6 or 6-6 bonds facing upward is from the majority of experimental observations.¹²⁻¹⁴ Therefore, purely different molecular orientations do not induce large enough differences in the electronic states to explain our experimental findings.

Thus, we must consider a model with local substrate reconstruction. While it has been agreed that the B molecule adsorbs on the nonreconstructed Ag(100) surface, it has been proposed that the D molecule adsorbs in a pit with four Ag atoms removed from the topmost substrate layer and one from the second layer (a five-atom pit, called Pit5).¹⁴ Placing an isolated C_{60} molecule in such a pit (with either 6-6 bond or edge atom adsorption) indeed results in a broadening of the LUMO state and a shift of the LUMO and LUMO+1 states towards the Fermi level [Fig. 4(c)] as compared with the results of a C_{60} molecule on perfect Ag(100) substrate (Pit0). Placing a C_{60} molecule in the pit with neighboring C_{60} molecules in a unit cell [Fig. 4(b), not a realistic unit cell but with positions similar to some local environment of the DM molecules in the STM images] retains the basic features of the isolated C_{60} molecule [Fig. 4(d)], indicating that the interaction with the substrate is much stronger than with neighboring C_{60} molecules and the basic electronic state features is dominated by the interaction with the substrate. From

FIG. 3. (Color online) Differently oriented C_{60} adsorption configurations on perfect Ag(100) surface and their corresponding DOS (including C_{60} -DOS and 6C-DOS). (a) configurations with 5-6 bond facing up and (b) their corresponding C_{60} -DOS and 6C-DOS; (c) configurations with 6-6 bond facing up and (d) their corresponding C_{60} -DOS and 6C-DOS.

symmetry considerations, we have also considered other types of pits. Changing the pit to only one Ag atom (Pit1) removed from the topmost layer produces similar DOS to that of a C_{60} molecule on a perfect surface (Pit0). A pit of only four Ag atoms (Pit4) removed from the topmost substrate layer can already result in similar DOS to that of Pit5.

Comparing with experimental dI/dV spectra [replotted in the inset of Fig. 4(c)], we can thus assign the DM molecule as adsorbed in a four-atom or five-atom pit, confirming the geometric origin of the BD contrast. Thus, our results unambiguously support the suggestion that the apparent BD contrast has a dominant geometric origin, as concluded from the ob-

FIG. 4. (Color online) (a) Ball models of a nonreconstructed Ag(100) surface (Pit0), 1-atom (Pit1), 4-atom (Pit4) and 5-atom (Pit5) pit; (b) configurations used for DM in a unit cell; (c) C₆₀-DOS and 6C-DOS for an isolated C₆₀ placed in different pit configurations shown in (a) and the experimental dI/dV curves for B and DM (inset); (d) C₆₀-DOS and 6C-DOS for DM in a unit cell shown in (b).

servation of Ag islands piling up near a C₆₀ island after annealing a sample prepared at low temperature.¹⁴ The calculated different electronic DOS for B and DM molecules indeed predicts a different BD contrast when imaged at either negative or positive bias voltages, consistent with experimental observation (Fig. 1).

C₆₀-C₆₀ dimer. Bringing two C₆₀ molecules to a distance of ~ 9.3 Å might induce a strong interaction to form bonds.^{14,27} The shortest C₆₀-C₆₀ distance observed in the STM images is ~ 9.4 Å for the two neighboring DD molecules. We thus consider the possibility of dimerization of the DD molecules. Two kinds of dimers, one with a single-bond (DD-I)²⁸ and another with a double-bond (DD-II)^{14,27} between the two C₆₀ molecules [Figs. 5(a) and 5(b)], were investigated by placing them into two neighboring five-atom pits with a separation of 8.67 Å along the [110] direction. Again, the chosen unit cell does not match the experimental observation but only mimics the local structure. The free-standing counterparts of these two dimers have been extensively studied previously using different level of theoretical approximations.^{28–30} The C₆₀-DOS and 6C-DOS are both plotted in Figs. 5(c) and 5(d). Compared to the DOS of a B

molecule adsorbed on a perfect surface in the same unit cells [Fig. 5(a)], both dimers still show a pronounced HOMO peak at -1.3 eV, but the LUMO+1 band is significantly broadened and only remains visible as a broad peak in the 6C-DOS. The LUMO band is also broadened and shifted towards the Fermi level in the C₆₀-DOS, but it becomes invisible in the 6C-DOS for DD-I. The difference in the 6C-DOS between DM and DD-I is that the LUMO band shows a small but visible peak for DM but no peaks for DD-I, indicating a stronger interaction between the two C₆₀ molecules in the dimer. While the nonrelaxed pits separate by only 8.67 Å, the C₆₀-C₆₀ distance for the two molecules in the relaxed geometry is found to be 9.26 Å for DD-I and 9.19 Å for DD-II. The good agreement between the calculated 6C-DOS and the dI/dV spectra, together with the good agreement in the C₆₀-C₆₀ distance, supports our proposed model of the formation of dimers, likely with a DD-I structure rather than a DD-II structure, although the calculation favors adsorption of the latter energetically to some extent.

The assignment of the DD-I instead of the DD-II structure to the DD molecule is further supported by the observed asymmetry in the nodal structure of the DD molecules [Fig.

FIG. 5. (Color online) (a) DD-I and (b) DD-II configurations in our calculations; (c) 6C-DOS and (d) C₆₀-DOS for DD-I and DD-II structures, and (inset) the experimental dI/dV for the DD molecules.

1(b)], namely, the two lobes in the same C₆₀ molecule have different brightness and the images of the two C₆₀ molecules within the same dimer have no mirror symmetry with respect to the plane bisecting them. As can be seen in Fig. 5(a), with the 6-6 bond facing upwards, this dimer DD-I indeed provides a broken symmetry between the two pentagons that are responsible for the two lobes in the nodal structure,^{12,14} consistent with the images. The observed asymmetry in Fig. 1 is not an artifact since no such asymmetry is found for DM in the same image and a similar asymmetry is observed in the

orthogonally oriented domains. With the two C₆₀ molecules sitting in two neighboring pits at a short distance of ~ 9.4 Å, comparable to the calculated equilibrium distance of 9.26 Å for C₆₀ polymerization,²⁷ it is not surprising that the surface strain energy and the thermal energy can induce dimerization.

Charge transfer. It is a challenge to analyze the charge transfer from dI/dV spectra that contain information only on the top portion of the C₆₀ molecules. The charge transfer has often been estimated by the band-filling of the C₆₀'s LUMO

FIG. 6. (Color online) (a) The integrated electron charge below the interface as a function of the moving interface position and (inset) a sketch of C_{60} in a five-atom pit with contour lines indicating the possible interface between C_{60} and the pit surface for the charge transfer calculations. (b) Calculated isodifferential electron density (white contours) at $6 \times 10^{-4} e/\text{\AA}^3$ for a C_{60} molecule in Pit0 and Pit5.

states through shifts of the LUMO (Refs. 9 and 17) or LUMO+1 (Ref. 31) bands. This is valid only if the interaction does not strongly modify the band shapes and change the energetic separation between the LUMO and LUMO+1 bands. As seen in Figs. 2 and 5, in the case of dimers, both the LUMO band and the LUMO+1 band are drastically distorted from those of the isolated C_{60} molecules. Thus, reliable estimates of the charge transfer from our experimental data become impossible. To calculate the charge transfer, we adopt a procedure devised by Lu *et al.*,¹⁶ in which an xy -integrated differential electron density curve against the z coordinate is plotted in order to determine the boundary between the C_{60} molecule and the substrate. In the case of a pit, a nonplanar interface that mimics the C_{60} geometry in the pit must be adopted [inset of Fig. 6(a)]. The curve in Fig. 6(a) gives the integrated electron charge below such an interface as a function of the z position of the interface for two C_{60} molecules in DD-I structure. The calculated maximum val-

ues of the charge transfer for B, DM, DD-I, and DD-II are, respectively, 0.07, 0.25, 0.17, and 0.18 electrons per C_{60} molecule. Our results for the B molecules are similar but smaller than what Lu *et al.* reported (0.15 e) for an isolated C_{60} molecule on Ag(100).¹⁶ For DM and DD, the stronger interaction with substrate indeed enhances the charge transfer. As seen from Figs. 6(b) and 6(c), the change in electron charge density is significantly larger and is over a bigger region for the C_{60} molecule placed in a five-atom pit than it on a perfect surface. Nevertheless, under all circumstances, our calculated values are still significantly less than those deduced from EELS (Ref. 8) and PES.⁹

Our experiments and simulations have clearly demonstrated the inhomogeneity and aperiodicity of the electronic properties of this C_{60} monolayer. This raises questions about the validity of the description of the energy band structure, which usually can only describe a periodic structure, of the C_{60} monolayer on Ag(100) and calls for reinterpretation of the photoemission spectroscopic data.^{9,10,15} Since PES is sensitive only to energy states below the Fermi level,^{9,17} only the LUMO states of DM and DD molecules may have been probed in those work. The deduced charge transfer must correspond to these molecules rather than to the full monolayer. The 0.9 electron transfer deduced from the LUMO band filling, rather than the 1.7 electron transfer deduced from linear extrapolations of K coverages at half and full LUMO band filling as reported in the same paper,⁹ may be much closer to reality. Our results also do not support the previous speculation of superconductivity in $C_{60}/\text{Ag}(001)$.

CONCLUSION

In conclusion, we have studied the morphologic and electronic structure of C_{60} monolayer on Ag(100) with both STM/STS measurements and first principles simulations. Our STM images and STS spectra confirm that the major BD contrast comes from geometric effect and the dim molecules are sitting in local pits induced by adsorption. In addition to the dim monomer C_{60} molecule, the measured dI/dV spectra and the calculated 6C-DOS indicate the formation of C_{60} dimer when two C_{60} molecules are sitting in two neighboring pits with a separation of 8.67 $\text{\AA}$. The charge transfer for B, DM, and DD molecules are quite different. All these evidence a highly inhomogeneous monolayer. Thus, we cannot expect a high superconducting T_c based on the low DOS near Fermi level and the inhomogeneous structure. The band structural analysis of this monolayer is also problematic.

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- ¹S. Modesti, S. Cerasari, and P. Rudolf, *Phys. Rev. Lett.* **71**, 2469 (1993).
- ²M. R. C. Hunt, S. Modesti, P. Rudolf, and R. E. Palmer, *Phys. Rev. B* **51**, 10039 (1995).
- ³M. K.-J. Johansson, A. J. Maxwell, S. M. Gray, P. A. Brühwiler, D. C. Mancini, L. S. O. Johansson, and N. Mårtensson, *Phys. Rev. B* **54**, 13472 (1996).
- ⁴K. D. Tsuei, J. Y. Yuh, C. T. Tzeng, R. Y. Chu, S. C. Chung, and K. L. Tsang, *Phys. Rev. B* **56**, 15412 (1997).
- ⁵C. T. Tzeng, W. S. Lo, J. Y. Yuh, R. Y. Chu, and K. D. Tsuei, *Phys. Rev. B* **61**, 2263 (2000).
- ⁶E. Giudice, E. Magnano, S. Rusponi, C. Boragno, and U. Valbusa, *Surf. Sci.* **405**, L561 (1998).
- ⁷G. Costantini, S. Rusponi, E. Giudice, C. Boragno, and U. Valbusa, *Carbon* **37**, 727 (1999).
- ⁸A. Goldoni, C. Cepek, E. Magnano, A. D. Laine, S. Vandrè, and M. Sancrotti, *Phys. Rev. B* **58**, 2228 (1998).
- ⁹A. Goldoni and G. Paolucci, *Surf. Sci.* **437**, 353 (1999).
- ¹⁰C. Cepek, I. Vobornik, A. Goldoni, E. Magnano, G. Selvaggi, J. Kröger, G. Panaccione, G. Rossi, and M. Sancrotti, *Phys. Rev. Lett.* **86**, 3100 (2001).
- ¹¹C. Cepek, R. Fasel, M. Sancrotti, T. Greber, and J. Osterwalder, *Phys. Rev. B* **63**, 125406 (2001).
- ¹²M. Grobis, X. Lu, and M. F. Crommie, *Phys. Rev. B* **66**, 161408(R) (2002).
- ¹³W. W. Pai and C. L. Hsu, *Phys. Rev. B* **68**, 121403(R) (2003).
- ¹⁴C. L. Hsu and W. W. Pai, *Phys. Rev. B* **68**, 245414 (2003).
- ¹⁵V. Brouet, W. L. Yang, X. J. Zhou, H. J. Choi, S. G. Louie, M. L. Cohen, A. Goldoni, F. Parmigiani, Z. Hussain, and Z. X. Shen, *Phys. Rev. Lett.* **93**, 197601 (2004); **95**, 099903(E) (2005).
- ¹⁶X. Lu, M. Grobis, K. H. Khoo, S. G. Louie, and M. F. Crommie, *Phys. Rev. B* **70**, 115418 (2004).
- ¹⁷W. L. Yang, V. Brouet, X. J. Zhou, H. J. Choi, S. G. Louie, M. L. Cohen, S. A. Kellar, P. V. Bogdanov, A. Lanzara, A. Goldoni, F. Parmigiani, Z. Hussain, and Z. X. Shen, *Science* **300**, 303 (2003).
- ¹⁸Y. Z. Li, M. Chander, J. C. Patrin, J. H. Weaver, L. P. F. Chibante, and R. E. Smalley, *Science* **253**, 429 (1991).
- ¹⁹P. Moriarty, M. D. Upward, A. W. Dunn, Y. R. Ma, P. H. Beton, and D. Teehan, *Phys. Rev. B* **57**, 362 (1998).
- ²⁰J. Schlappa, C. Schüßler-Langeheine, R. Scherer, and L. H. Tjeng, *Phys. Rev. Lett.* **93**, 119701 (2004).
- ²¹O. Gunnarsson, *Rev. Mod. Phys.* **69**, 575 (1997).
- ²²G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ²³P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- ²⁴J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ²⁵G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ²⁶P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- ²⁷J. Nakamura, T. Nakayama, S. Watanabe, and M. Aono, *Phys. Rev. Lett.* **87**, 048301 (2001).
- ²⁸G. E. Scuseria, *Chem. Phys. Lett.* **257**, 583 (1996).
- ²⁹J. Kürti and K. Németh, *Chem. Phys. Lett.* **256**, 119 (1996).
- ³⁰K. S. Kim, J. M. Park, J. Kim, S. B. Suh, P. Tarakeshwar, K. H. Lee, and S. S. Park, *Phys. Rev. Lett.* **84**, 2425 (2000).
- ³¹R. Yamachika, M. Grobis, A. Wachowiak, and M. F. Crommie, *Science* **304**, 281 (2004).