Optimal Electron Doping of a C$_{60}$ Monolayer on Cu(111) via Interface Reconstruction

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We demonstrate the charge state of C$_{60}$ on a Cu(111) surface can be made optimal, i.e., forming C$_{60}^{3-}$ as required for superconductivity in bulk alkali-doped C$_{60}$, purely through interface reconstruction rather than with foreign dopants. We link the origin of the C$_{60}^{3-}$ charge state to a reconstructed interface with ordered (4 × 4) 7-atom vacancy holes in the surface. In contrast, C$_{60}$ adsorbed on unreconstructed Cu(111) receives a much smaller amount of electrons. Our results illustrate a definitive interface effect that affects the electronic properties of molecule-electrode contact.

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In bulk fulleride $A_x$C$_{60}$ ($A = \text{Na, K, etc.}$) [1], an “optimal doping” state favoring superconductivity is known to occur for $n = 3$, with 3 electrons on each C$_{60}$ (C$_{60}^{3-}$). Since C$_{60}$ films on metallic surfaces typically involve substrate-to-C$_{60}$ electron transfer that partially populates the C$_{60}$ lowest unoccupied molecular orbital (LUMO), it has been of great interest to pursue optimally doped C$_{60}$ films. Earlier studies show that the electron transfer amount does not simply depend on the substrate work function [2]. This raises the question of the role of the C$_{60}$/metal interface structure. Although strong C$_{60}$/metal interactions are not expected for, e.g., C$_{60}$ on noble metal surfaces, there is increasing evidence of C$_{60}$-induced interface reconstruction for C$_{60}$/Au(110) [3], C$_{60}$/Pt(111) [4], C$_{60}$/Al(111) [5], C$_{60}$/Ag(100) [6], and even for C$_{60}$/Ag(111) [7] and C$_{60}$/Cu(111) [8], etc. The typical scenario is that C$_{60}$ tends to dig a “vacancy” in the surface. Calculations, including our own, show this geometry increases the adsorption strength that compensates the energy cost of vacancy creation. No studies, however, have discussed how the electronic structure and hence the charge state of a C$_{60}$ film on a surface, are likely rooted in the application of an incorrect interface model. For C$_{60}$/Cu(111), it has been measured to range from 1–3 electrons per C$_{60}$ by photoemission spectroscopy (PES) [9]. Calculations predict a much smaller amount, <0.8e$^-$, for an unreconstructed interface [10]. The electronic band structure measured by a recent PES study is also at odds with theoretical analysis under the same assumption [11]. These conflicts are resolved by our ordered (4 × 4) 7-atom vacancy interface model. Because the structure can be alternatively viewed as having 9 Cu adatoms per unit cell at C$_{60}$ exohedral sites, the C$_{60}$ molecules can also be understood as doped by Cu adatoms.

The substrate-to-C$_{60}$ electron transfer have been roughly estimated from the softening of C$_{60}$ vibration modes [12], LUMO peak intensity in PES, etc. The most precise measurement would be a complete band mapping from angle-resolved (AR)PES. We have thus prepared well-ordered monolayer C$_{60}$ films and mapped the bands at 30 K. The C$_{60}$ film was obtained by depositing excess C$_{60}$, followed by annealing at 570 K to eliminate C$_{60}$ multilayers. The PES spectra were taken at U9-CGM (NSRRC, Taiwan) with a Scienta SES-200 hemispherical analyzer with a collecting angle of ±8°, a photon energy of 31.5 eV for AIPES and 22 eV for ARPES, and an overall energy resolution of 12 meV. Figure 1(a) depicts the Fermi surface (FS) with a ±20 meV energy integration window. At least two regions of FS crossing were observed around the $\bar{\Gamma}$ and $\bar{K}$ points. Figure 1(b) shows the band dispersion along $\bar{\Gamma}$-$\bar{M}$ and $\bar{\Gamma}$-$\bar{K}$. There is an occupied state around $\bar{\Gamma}$, generating an electronlike FS. Another FS crossing occurs near $\bar{K}$ and is attributed to hololike band dispersion. In Fig. 1(c), this hololike band dispersion is manifested in the measured momentum distribution curves (MDC). There are actually two FS crossings near $\bar{K}$ along $\bar{\Gamma}$-$\bar{K}$-$\bar{M}$ at $k_{\parallel} \approx 0.27 \text{ Å}^{-1}$.
Cu is thus \( C_{24} \) K per unit cell. The total amount of electron transfer from \( C_{22} \) near the accuracy of the extracted band position. (c) Measured MDC spectra vs doping time (fitted positions of the two holelike dispersive bands. (d) AIPES LUMO intensity at the Fermi energy (EF) was obtained after \( \sim 2600 \) s of dose time, a linear extrapolation shows that only \( \sim 0.1 \) K atom per \( C_{60} \) is required to render the 1 ML \( C_{60} \) film optimally doped. Consequently, each \( C_{60} \) already accepts \( \sim 2.9e^- \) from the Cu(111) substrate, consistent with the ARPES result.

Various electron transfer values for \( C_{60} \) on Cu(111) have been reported in experiments [9,11,12]. Here, we confirm the extraordinary \( \sim 3e^- \) charge transfer, being the largest value reported for undoped \( C_{60} \) monolayers. By using scanning tunneling microscopy and spectroscopy (STM/STS), we show that this charge transfer is related to interface reconstruction. STM and STS were conducted with a commercial Omicron variable-temperature microscope and a low-temperature microscope housed in two chambers with a base pressure \(< 4 \times 10^{-11} \) Torr. In our previous studies [8,16], we prepared “core-shell” islands with a two-stage method by first depositing \( C_{60} \) at \( \sim 500 \) K (for the “core” with a reconstructed interface) and then \( C_{60} \) at \( \sim 250 \) K (for the “shell” with an unreconstructed interface). A typical core-shell \( C_{60} \) island is shown in Fig. 2(a).

STS spectra taken at 77 K showed that the LUMO peak in the shell region was located \( \sim 0.75 \) V above \( E_F \) [dashed line, Fig. 2(b)], indicating a minor charge transfer. If the LUMO peak is approximately symmetric and has a peak position at \( E_F \), the band can be viewed as half-filled. In the core region, the LUMO peak shifts to a position slightly above \( E_F \) (solid line). This suggests that nearly \( \sim 3e^- \) are transferred to each \( C_{60} \), consistent with the PES results.

Strong chemical bonding between \( C_{60} \) and Cu(111) must have occurred to facilitate the observed large charge transfer. In order to investigate the bonding, we studied the interface structure in details. In Fig. 2(a), the STM topographic height of the core region is \( \sim 2 \) Å lower than and \( 0.35 \) Å\(^{-1}\) (also at \( 0.52 \) Å\(^{-1}\) and \( 0.46 \) Å\(^{-1}\)), as denoted by the green and the blue circles. The circles are fitted Lorentzian peak positions of the holelike band dispersion near the FS crossings. The amount of electron transfer is calculated by the Luttinger volume of the occupied FS area [13]. Assuming circular bands crossing near \( \Gamma \) and \( K \), there are \( \sim 0.09 \) electrons for the electron pocket around \( \Gamma \) and \( \sim 1.09 \) plus \( \sim 1.82 \) electrons for the two holelike bands near \( K \) per unit cell. The total amount of electron transfer from Cu is thus \( \sim 3 \) electrons per \( C_{60} \). This renders the \( C_{60} \) LUMO half-filled, and the \( C_{60} \) film is therefore nearly “optimally doped.” We also verified this extraordinary electron transfer using angle-integrated (Al)PES. The AlPES LUMO intensity at the Fermi energy (\( E_F \)) was tracked as potassium (K) atoms evaporated from a calibrated SAES getter source were incorporated into a \( C_{60} \) monolayer. The optimally doped (“\( K_{2}C_{60}, C_{60}^{3-} \)” and fully doped (“\( K_{3}C_{60}, C_{60}^{5-} \)” states have maximum and zero LUMO intensity at \( E_F \), respectively [14,15]. Figure 1(d) depicts the evolution of AlPES spectra with K doping, and its inset shows the spectra intensity at \( E_F \) vs K doping time. We note that the “\( K_{2}C_{60} \)” state was achieved with very slight K doping (\( \sim 90 \) s of dose time). Since “\( K_{3}C_{60} \)” was obtained after \( \sim 2600 \) s of dose time, a linear extrapolation shows that only \( \sim 0.1 \) K atom per \( C_{60} \) is required to render the 1 ML \( C_{60} \) film optimally doped. Consequently, each \( C_{60} \) already accepts \( \sim 2.9e^- \) from the Cu(111) substrate, consistent with the ARPES result.

FIG. 1 (color). (a) Fermi surface (FS) mapping of 1 ML \( C_{60} \). At least two regions of FS crossings were observed around \( \Gamma \) and \( K \). (b) Band dispersion along \( \Gamma - M \) and \( \Gamma - K \). FS crossings are marked by three pairs of colored triangles. The white circles denote the calculated LUMO-derived bands and the white dashed line is a guide to the eyes. The size of the circles indicates the accuracy of the extracted band position. (c) Measured MDC near the \( K \) point at various binding energies. The circles are the fitted positions of the two holelike dispersive bands. (d) AIPES spectra vs doping time (\( t_d \)) for the first five studied \( t_d \). As K atoms are doped, the LUMO peak shifts to higher binding energy. The inset shows the LUMO intensity at \( E_F \) vs \( t_d \).

FIG. 2 (color). (a) A “core-shell” island (35 nm \( \times \) 35 nm). (b) STS spectra show a dramatic shift of the LUMO band in the reconstructed core vs unreconstructed shell region. \( T = 77 \) K. (c) Calculated \( C_{60} \) PDOS of the unreconstructed and reconstructed (r-fcc) \( C_{60}/Cu(111) \) with 0.1 eV Gaussian broadening. The inset of (a) shows no energy gap near \( E_F \) in STS at \( \sim 5 \) K.
that of the shell region [8]. This large height difference suggests that the interface must have enough missing atoms to let a C_{60} “sink” by ~2 Å [17]. The number of missing Cu atoms, N, in a (4 × 4) unit cell can be obtained from a mass-flow analysis by in situ STM monitoring of C_{60} growth. This number is critical because it allows us to readily rule out implausible models. Our conclusion is that N ~ 7.1 ± 0.7 [17], thus leaving 9 out of 4 × 4 = 16 atoms per unit cell if the 7 atoms are removed from the outermost Cu layer.

A straightforward reconstructed interface model with a top layer Cu atom density of 9/16 is an ordered nanotemplate of 7-atom monolayer holes [Fig. 3(a)], in which strings of top layer Cu atoms are arranged in the kagome lattice. Previous experiments with STM [8,18] and x-ray strings of top layer Cu atoms are arranged in the kagome template of 7-atom monolayer holes [Fig. 3(a)], in which photoelectron diffraction (XPD) [19] implied a

In the Fig. 3(a) model, the

Inset: a typical LEED pattern.

(b) Selected LEED I-V beams and their tensor LEED fitting. Inset: a typical LEED pattern.
closest bottom C(1) atoms are $\sim 2.25$ Å (theory) and $\sim 2.20$ Å (LEED). The consistent trend of shorter Cu-C bond lengths in the best-fit LEED model suggests that $C_{60}$ is bonded closer to the Cu substrate than theory predicts. The various C and Cu(A, B) bond lengths result in alternating clockwise and counterclockwise Cu(A, B) hexamer (red solid line) rotation on a honeycomb sublattice and a distorted Cu(A) hexagon (white dashed line) that collaboratively enhance $C_{60}$-Cu bonding. To our knowledge, $C_{60}$ is the first known intact molecule to cause extensive reconstruction of Cu(111). This special structural stability derives from an intricate matching of the Cu lattice spacing, the $(4 \times 4)$ ordering, the $C_{60}$ orientation, and the top Cu layer distortion, and it is quite unique and remarkable. Based on our interface model, we recalculated the partial density of states (PDOS) and band dispersion to compare with the STS and PES data. $C_{60}$ PDOS curves for both the unreconstructed and reconstructed r-fcc models are shown in Fig. 2(c). The $C_{60}$ molecular orbital band energies obtained for the unreconstructed case are similar to previous theoretical results [10] and the limited LUMO occupancy indicates an estimated electron transfer $< 1e^-/C_{60}$. In the r-fcc model, the LUMO-derived band energy is lowered by 0.35 eV and is near the Fermi level and nearly half-filled, indicating a charge transfer of $\sim 3e^-/C_{60}$ in excellent agreement with PES and STS. Note that the overall band intensity suppression and band width broadening in the r-fcc model indicate strong $C_{60}$ and Cu(111) interactions. The band dispersion was also analyzed theoretically [Fig. 1(b)]. The LUMO-derived bands were extracted by analyzing the carbon-projected electron density. The band maximum appears very near $E_F$ at $\vec{k}$ and the bands lie well below $E_F$ elsewhere in the surface Brillouin zone; both are in agreement with the experiments. The calculation is however unable to clearly distinguish two separate hole bands, unlike the MDC in Fig. 1(c). For the unreconstructed interface, such a hololike band is completely missing. Another state that disperses downward from $\vec{\Gamma}$ (yellow dotted line) was observed in ARPES [Fig. 1(b)]. This band was previously attributed to an anisotropic interface state [11]. Our calculations find it contains significant carbon contribution around $\vec{\Gamma}$. In optimally alkali-doped bulk $C_{60}$ fullerides, e.g., “$K_3C_{60}$,” superconductivity has been observed [1]. We tested our alkali-free and optimally doped $C_{60}$ monolayer for 2D surface superconductivity [20]. With STS, we found no sign of an energy gap down to $\sim 5$ K [Fig. 2(a) upper inset]. Likely, the ultrathin thickness [21] and the triangular symmetry of a $C_{60}$ monolayer tend to prohibit Cooper pair formation. A surface superconductivity transition, if present, must have been suppressed to an even lower temperature. We expect our study to spawn further investigations of $C_{60}$/Cu(111) for 2D superconductivity.

Finally, it indeed takes a combination of techniques and theoretical analysis to unambiguously determine the $C_{60}$-substrate interface structure. Our calculated $C_{60}$ STM images (not shown) vary only slightly with reconstruction. STS-PDOS, ARPES, and the total energy are all sensitive to reconstruction, but cannot clearly distinguish the r-fcc and r-hcp models. Ultimately, it is the LEED I-V analysis that confirms the r-fcc model. The 7-atom vacancy holes observed in $C_{60}$/Cu(111) interface are much larger than the single-vacancy holes previously observed [4,7]. We believe the more corrugated $C_{60}$/Cu(111) interface allows more intimate substrate-molecule contact and is likely the key of “adatom self doping” that renders $C_{60}$ optimally doped. Our endeavor to elucidate doping-structure correlation at a molecular-substrate interface adds a new dimension in understanding functional molecular thin films.

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