Optimal Electron Doping of a C60 Monolayer on Cu(111) via Interface Reconstruction

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We demonstrate the charge state of C₆₀ on a Cu(111) surface can be made optimal, i.e., forming C₆₀³⁻ as required for superconductivity in bulk alkali-doped C₆₀, purely through interface reconstruction rather than with foreign dopants. We link the origin of the C₆₀³⁻ charge state to a reconstructed interface with ordered (4 × 4) 7-atom vacancy holes in the surface. In contrast, C₆₀ 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 AₓC₆₀ (A = Na, K, etc.) [1], an “optimal doping” state favoring superconductivity is known to occur for n = 3, with 3 electrons on each C₆₀ (C₆₀³⁻). Since C₆₀ films on metallic surfaces typically involve substrate-to-C₆₀ electron transfer that partially populates the C₆₀ lowest unoccupied molecular orbital (LUMO), it has been of great interest to pursue optimally doped C₆₀ 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 C₆₀/metal interface structure. Although strong C₆₀-metal interactions are not expected for, e.g., C₆₀ on noble metal surfaces, there is increasing evidence of C₆₀-induced interface reconstruction for C₆₀/Au(110) [3], C₆₀/Pt(111) [4], C₆₀/Al(111) [5], C₆₀/Ag(100) [6], and even for C₆₀/Ag(111) [7] and C₆₀/Cu(111) [8], etc. The typical scenario is that C₆₀ tends to dig a “vacancy” in the surface. Calculations, including our own, show this geometry increases the adsorption strength and compensates the energy cost of vacancy creation. No studies, however, have discussed how the electronic structure and hence the charge state of a C₆₀ film are affected by its interface structure. Here, we discovered that a C₆₀ monolayer on Cu(111) is optimally electron doped purely by interface reconstruction and without intercalating alkali atoms. We convincingly establish the C₆₀³⁻ charge state and trace its origin to a reconstructed interface with ordered (4 × 4) large 7-atom vacancy holes in the surface. The key link between molecular doping and a reconstructed interface indicates the practical needs of tackling the often neglected difficult interface structure problems which could prove essential in understanding the physics and chemistry of thin film materials.

Many inconsistencies between experiment and theory in heteroepitaxial systems, such as the charge state of a C₆₀ film on a surface, are likely rooted in the application of an incorrect interface model. For C₆₀/Cu(111), it has been measured to range from 1–3 electrons per C₆₀ 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 C₆₀ exohedral sites, the C₆₀ molecules can also be understood as doped by Cu adatoms.

The substrate-to-C₆₀ electron transfer have been roughly estimated from the softening of C₆₀ 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 C₆₀ films and mapped the bands at 30 K. The C₆₀ film was obtained by depositing excess C₆₀, followed by annealing at 570 K to eliminate C₆₀ 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 Γ and K points. Figure 1(b) shows the band dispersion along Γ-M and Γ-¯K. There is an occupied state around Γ, generating an electronlike FS. Another FS crossing occurs near 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 K along Γ-¯K-M at k┴ ∼ 0.27 Å⁻¹.
doping, and its inset shows the spectra intensity at $E_F$ vs K doping time. We note that the “K$_6$C$_{60}$” state was achieved with very slight K doping (~90 s of dose time). Since “K$_4$C$_{60}$” was obtained after ~2600 s of dose time, a linear extrapolation shows that only ~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 ~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 ~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 × 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 ~500 K (for the “core” with a reconstructed interface) and then C$_{60}$ at ~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 ~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 ~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 ~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 hololike 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 ~0.09 electrons for the electron pocket around $\Gamma$ and ~1.09 plus ~1.82 electrons for the two hololike bands near $K$ per unit cell. The total amount of electron transfer from Cu is thus ~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 (AI)PES. The AIPES 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$_4$C$_{60}$, C$_{60}$”$^3$”) and fully doped (“K$_2$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 AIPES spectra with K

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 $\Gamma-\bar{M}$ and $\Gamma-\bar{K}$. 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 and (d) Lorentzian peak positions of the holelike band dispersion 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 x 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 ~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 $\sim$2 Å [17]. The number of missing Cu atoms, $N$, in a $(4 \times 4)$ 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 $N \sim 7.1 \pm 0.7$ [17], thus leaving 9 out of $4 \times 4 = 16$ 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 photoelectron diffraction (XPD) [19] implied a C$_{60}$ orientation with its hexagonal ring facing down and two coexisting high-symmetry azimuthal orientations differing by 60°. The combined substrate-C$_{60}$ orientation is characterized by C$_3$ symmetry. The Fig. 3(a) model adopts this experimentally determined C$_{60}$ orientation. Our ab initio calculations estimate that the reconstruction model is favored by $\sim$0.2 eV/cell over the unreconstructed case [17]. In the Fig. 3(a) model, the C$_{60}$ center can either sit at an fcc or an hcp site, depending on whether the top layer Cu atoms are stacked at unaffected fcc or faulted hcp sites. Henceforth, we denote these two reconstructed cases as the r-fcc and r-hcp models. Our calculations give very similar energies for the two structures. There is a slight preference for hcp-site C$_{60}$ adsorption ($\sim$0.01 eV/cell lower) if the slab used in the calculation is thinner than $\sim$15 Cu layers. For thicker slabs (from 18 to 30 Cu layers), the r-fcc structure becomes $\sim$0.02 eV/cell lower in energy. A large barrier, $\sim$0.5 eV/cell, prevents a transition between the r-fcc and r-hcp structures. The azimuthal C$_{60}$ rotation barrier is large, i.e., $\sim$2 eV. When the interface is left unreconstructed, C$_{60}$ preferably adsorbs at hcp sites by $\sim$0.02 eV/cell, consistent with a previous calculation [10].

We performed an extensive tensor LEED I-V curve fitting to a very large experimental database for quantitative structure determination. Experimental I-V curves were extracted with code developed in-house. The LEED analysis was performed with our symmetrized automated tensor LEED code [17]. A total energy fitting range of $\sim$3500 eV was used to evaluate the Pendry $R$ factor. We used 33 independent beams taken at room temperature between 20 and 210 eV to fit 102 independent parameters. Initial test structures were based on fully relaxed theoretical coordinates. Test models with C$_{60}$ orientations clearly inconsistent with the STM and XPD were excluded. Two mirror domains of azimuthal C$_{60}$ orientation are mixed with equal weight because the experimental LEED pattern shows C$_{3v}$ symmetry instead of the C$_3$ symmetry of a single C$_{60}$ domain. We optimized both the (a) unreconstructed and the (b) reconstructed interface models. The best LEED Pendry $R$ factors are (a) 0.330 versus (b) 0.572 before optimization. After optimization, we obtained (a) 0.324 versus (b) 0.274. The $\sim$17% difference in $R$ factors shows that interface reconstruction is clearly favored. Furthermore, we compared the faulted r-hcp model with the unfaulted r-fcc reconstructed model. Before optimization, the Pendry $R$ factors are (r-hcp) 0.568 versus (r-fcc) 0.572. After optimization, we obtained (r-hcp) 0.304 versus (r-fcc) 0.274. The $\sim$11% difference indicates that the r-fcc model is preferred. The single adsorption site of C$_{60}$, as determined here by LEED, was inferred previously from our STM study [8] but is at odds with an earlier STM result [18]. In C$_{60}$/Pt(111) [4] and C$_{60}$/Ag(111) [7], a C$_{60}$ is found to reside atop a single atom vacancy, rather than a 7-atom vacancy. We also tested this unlikely single-vacancy model. The optimized $R$ factor is 0.406 and is clearly unfavorable. Compared with a recently published LEED determination of C$_{60}$/Ag(111) [7] with an $R$ factor of 0.36, our analysis yields an $R$ factor of $\sim$0.27. Figure 3(b) shows selected measured and fitted LEED I-V curves.

Our LEED analysis and ab initio results illustrate a salient structural feature: the strong Cu-C$_{60}$ bonding is enhanced not only by pulling a C$_{60}$ into a Cu “bowl,” but also by significantly distorting the top Cu layer. In Fig. 3(a), there are several short C-Cu bonds. We denote the red Cu atoms as Cu(A), yellow Cu atoms as Cu(B), and the bottom Nth layer C atoms as C(N), where C(1) is the bottom C hexagon. The Cu(A)-C(2) bonds are the shortest, with an average bond length of 2.10 Å (theory) and 1.98 Å (LEED). The other strong Cu-C bonds are Cu(A)-C(4) and Cu(B)-C(3), with bond lengths of 2.40 and 2.31 Å, respectively (theory), and 2.30 Å and 2.14 Å (LEED). The bond lengths between the second layer Cu atoms (green) and the

![Figure 3](image-url)
lar symmetry of a
inset]. Likely, the ultrathin thickness [21] and the triangu-
(C60
theoretical analysis to unambiguously determine the
bands were extracted by analyzing the carbon-projected
electron density. The band maximum appears very near EF
at K and the bands lie well below EF 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 holelike
band is completely missing. Another state that disperses
downward from Γ (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 Γ.
In optimally alkali-doped bulk C60 fullerides, e.g.,
"K3C60," superconductivity has been observed [1]. We
tested our alkali-free and optimally doped C60 monolayer
for 2D surface superconductivity [20]. With STS, we found
no sign of an energy gap down to ~5 K [Fig. 2(a) upper
inset]. Likely, the ultrathin thickness [21] and the triangular
symmetry of a C60 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 inves-
tigations of C60/Cu(111) for 2D superconductivity.
Finally, it indeed takes a combination of techniques and
theoretical analysis to unambiguously determine the
C60-substrate interface structure. Our calculated C60 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 C60/Cu(111) interface are much larger than the
single-vacancy holes previously observed [4,7]. We
believe the more corrugated C60/Cu(111) interface allows
more intimate substrate-molecule contact and is likely the
key of "adatom self doping" that renders C60 optimally
doped. Our endeavor to elucidate doping-structure corre-
lation at a molecular-substrate interface adds a new dimen-
sion in understanding functional molecular thin films.
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tails on calculations and STM mass flow analysis.