ELECTRONIC PROPERTIES OF STRONGLY RESHAPED ORGANIC-METAL INTERFACES

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The formation of self-assembled nanostructure on a surface results from a subtle equilibrium between the attractive intermolecular forces and the forces that drive molecules to the substrate. In the case of strong molecule-substrate interactions, molecules can even induce nanoscale surface reshaping, which is now a promising field in materials engineering [1]. In this work, we study the electronic properties of strongly reconstructed organic-metal interfaces using *ab initio* calculations and scanning tunneling microscopy (STM) simulations.

For the electronic structure calculations, we have used the density functional theory (DFT) within a local density approximation (LDA) included in the SIESTA package [2]. DFT-LDA calculations provided fully optimized geometries for each system under study along with their deformation and adsorption energy, density of states (DOS), Mulliken population analysis, and charge density. We also performed STM simulations with our SPAGS-STM (Strongly Parallel Adaptive Grid Solvers – STM) software. The software includes several algorithmic strategies such as parallel computation of the tunnel currents [3] and adaptive grids that minimize the probing sites needed to obtain a high resolution image [4]. In the simulations, the tunnel currents were computed within a scattering approach based on the Landauer-Büttiker formalism along with an extended Hückel theory Hamiltonian originally developed by Cerdá *et al* [5]. The good accuracy of our theoretical method will be shown by comparing a series STM images and dI/dV spectra with experimental data of Lu *et al* [6] on the adsorption of isolated C_{60} on the Ag(100) surface.

With these computational tools, we will address a recent and captivating STM investigation in which the adsorption of tetracyanoethylene (TCNE) molecule leads to striking behaviors on various noble metals [7]. More precisely, TCNE molecules on a Cu(100) surface are self-assembled into monolayer chains and islands where specific Cu atoms near these nanostructures appear strongly buckled. As shown in Fig. 1(a), DFT-LDA calculations predict a strong reconstruction of the Cu(100) surface, where high buckled Cu atoms rise more than 1 Å over the topmost plane. The surface buckling can be associated to a deformation energy of 3.55 eV. Also, a strong molecular bonding to the Cu surface is observed, where at least an energy of 1.65 eV is needed to break a single Cu-N bond. The generated STM image in Fig. 1(b) displays a good concordance with the experimental one and confirms the strong buckling of the Cu(100) surface around TCNE nanostructures. Mulliken population analysis clearly indicates a charge transfer of 0.4 *e* to the TCNE molecule. Other evidences of charge transfer from the high buckled Cu atoms to the TCNE molecule that are based on the shape and on the displacement of peaks observed in DOS will be also presented. These results suggest that TCNE self-assemblies could be used to design charge transfer compounds for molecule-based magnetic devices.

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Figures:

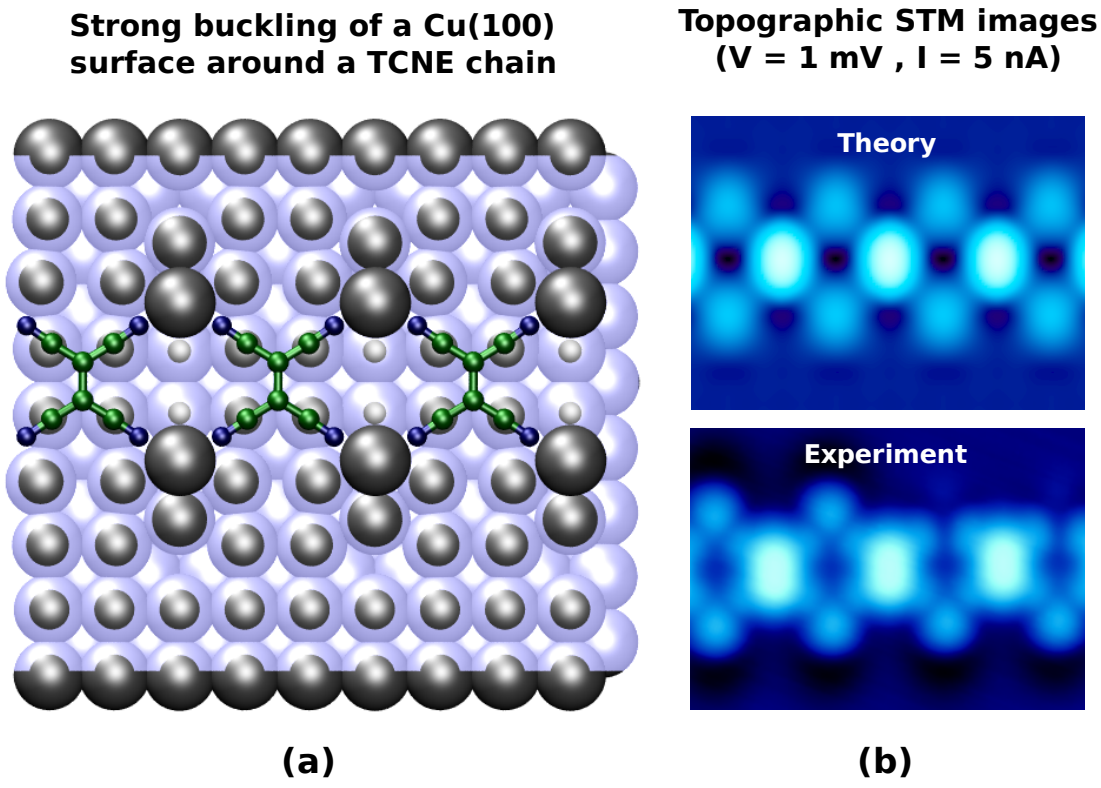

FIG. 1 – (a) DFT-LDA optimized structural geometry for a highly buckled Cu(100) surface around a TCNE chain. A transparent plane is used to guide the eye on the strong reconstruction of the topmost Cu layer. (b) Comparison between topographic STM images of (top) the theoretical model using the SPAGS-STM software and (bottom) experimental data from Ref. [7].