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A long-range ordered array of copper tetrameric units embedded in an on-surface metal organic framework

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We report on the assembly of a highly-ordered array of copper tetrameric clusters, coordinated into a metal-organic network. The ordered cluster array has been achieved by deposition of tetrahydroxyquinone molecules on the Cu(111) surface at room temperature, and subsequent thermally activated dehydrogenation with formation of tetraoxyquinone tetra-anions with a 4×4 periodicity. The supramolecular organic network acts as spacer for the highly ordered two-dimensional network of copper tetramers at the very surface.

Adsorption of single molecular units on surfaces towards fabrication of supramolecular structures is one of the most promising ways for obtaining novel two-dimensional (2D) ordered metal-organic architectures,[1] with unique and peculiar structural features, functionalities and catalytic properties.[2–8] In this way, single metal atoms embedded into an organic cage[9,10] or small metal clusters[11,12] can be obtained in a highly ordered fashion within a quasi-planar 2D molecular lattice. For metals like gold, clusters made of few atoms often present catalytic properties absent in their bulk counterpart,[13] as also the

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chemical reduction efficiency of tetrameric copper clusters has been recently outlined.[14] The wide range of applications that need specific cluster size underlines the importance of developing novel techniques in order to enable the tuning of properties of the materials.

The variety of the existing techniques to produce clusters on a surface spans from wet-chemistry,[15] to atomic beam deposition,[16] to assisted chemical vapor deposition,[17] to atomic cluster sources,[14] to soft-landing of size-selected gas phase clusters onto supported surfaces,[18] though a long-range highly-ordered cluster distribution is not ensured. Electronic, optical and magnetic properties are deeply related to the metal clusters size. In addition, recent evidences also show that a precise control of the registry between the surface-supported metal centers and the substrate guaranteed by long-range order can have a dramatic influence on their catalytic properties.[19] Thus, controlling cluster size and distribution acquires a pivotal role when tailoring such properties. Metal surface coordination networks to-date are typically composed by single metal atom centers or limited to trimers.[11] In this work, we present a novel method to produce size-selected copper tetramers by the employment of tetrahydroxyquinone (THQ) as the organic template obtaining a metal-organic network. The organic template serves as a mold to embed monodispersed copper tetrameric units of precise size and shape, in a long-range ordered network.

I. EXPERIMENTAL AND THEORETICAL DETAILS

Preparation and characterization of the samples have been performed under ultrahigh vacuum (UHV) conditions in two different experimental chambers, with base pressure in the low 10^{-10} mbar range, with the same main ancillary facilities for sample preparation.

The Cu(111) single crystal was cleaned by multiple cycles of 1 keV Ar^+ sputtering and annealing at ∼725 K until a clean surface was obtained with large terraces, as confirmed by scanning tunneling microscopy (STM) imaging. Commercially available THQ molecules were deposited from a home-made quartz crucible evaporator held at ∼375 K. No significant increase in the baseline pressure of the chamber was observed during evaporation. Degassing of the molecules was performed prior to evaporation for several hours at a temperature lower than the sublimation one. During deposition the surface was always held at room temperature (RT), and the dehydrogenation was activated by subsequent thermal annealing. The annealing procedure was performed through a 20 minutes heating ramp up to ∼385 K followed by four minutes annealing at the same temperature.

The x-ray photoelectron spectroscopy (XPS) data were acquired at room temperature, at the ALOISA beamline of the synchrotron light source ELETTRA in Trieste (Italy).[20,21] The photoemission data were collected by means of a hemispherical electron energy analyzer in normal emission while keeping the sample at grazing incidence (∼4°), with photon energies of 450 eV (C 1s) and 650 eV (O 1s). The binding energy of the core-level spectra was carefully calibrated by alignment with respect to the Fermi level of the copper substrate as absolute reference.

STM images have been acquired with an Omicron scanning tunneling microscope (VT-STM). All of the STM measurements were executed at room temperature in constant-current mode using an electrochemically etched Pt - Ir tip. Typically, sample bias values between -1 V and +1 V have been adopted, and tunneling currents from 1 up to about 70 nA have been used. The STM data were processed with the WSxM software.[22] Fast Fourier Transform (FFT) filtering was applied to reduce the noise in the images.

Reflection High-Energy Electron Diffraction (RHEED) and Low-Energy Electron-Diffraction (LEED) measurements were performed at ALOISA and at the University of Padua, respectively, to check the formation of the 4×4 phase in the different chambers.

All Density Functional Theory (DFT) calculations and data post processing were carried out with the Quantum-ESPRESSO software package.[23] Ultrasoft pseudopotentials[24] and PBE-GGA exchange-correlation[25] were used. The wavefunction energy cutoff was set to ∼408 eV. The Brillouin zone was sampled at the Γ point, and dipole correction was applied to all on-metal calculations.[26] The Cu(111) surface was modelled by a three-layered slab with ∼18 Å of vacuum between periodic replicas. The force convergence threshold for structure optimisation was set to 0.025 eV/Å (the bottom Cu layer was constrained to the bulk positions). Simulated STM images were rendered using the Tersoff-Hamann method.[27]

II. RESULTS AND DISCUSSION

The THQ molecules (sketched in Fig. 1a) deposited on the Cu(111) surface held at room temperature and annealed up to ∼385 K, self-assemble into extended and single-domain islands, as revealed by the STM image shown in Fig. 1b. These islands present a 4×4 periodicity, corresponding to an intermolecular distance of 10.2 Å, as revealed by Low Energy Electron Diffraction (Fig. 1d) and in agreement with the Fast Fourier Transform (FFT) of the STM image

(Fig. 1b,c).

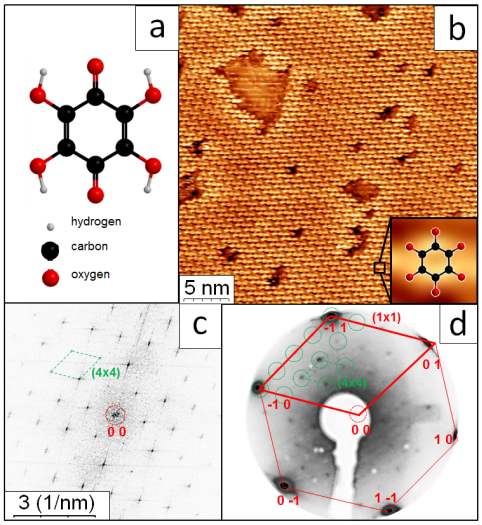

FIG. 1. (a) Ball and stick model of a THQ molecule; (b) large scale STM image (bias = 0.55 V; I = 37.2 nA) showing the self-assembly of TOQ tetra-anion on Cu(111) after annealing to ∼385 K; the TOQ tetra-anion is shown in the bottom right corner; (c) corresponding Fast Fourier Transform (FFT) image, and (d) low-energy electron-diffraction pattern acquired at an energy of 45 eV on the same sample.

Individual molecular units appear in the STM images as doughnut-like protrusions (see also Fig. 2a), with a size compatible with that of a single molecule, and with an intermolecular distance equal to four times the interatomic copper distance. The homogeneity in the apparent height of the doughnut-like structures points toward a flat adsorption geometry of the molecules, with the molecular ring parallel to the Cu(111) plane. High-resolution STM images show that additional apparently triangular features are present between the doughnuts (Fig. 2a). These additional features do not appear as triangles if defects are present in the molecular network, thus suggesting that the dominant triangular-shaped structure is present only when it is surrounded by three molecules (Supplementary Material, SM, Fig. S1). These features can be associated to thermally released copper adatoms incorporated in a metal-organic network by 2,3,5,6-tetraoxyquinone tetra-anion (TOQ) units, deriving from the quadruple dehydrogenation of the THQ molecules after the annealing procedure (see molecular models in Fig. 3). The azimuthal orientation of the tetra-anions determines the formation of two different chiral assemblies, with identical TOQ adsorption sites and 4×4 LEED pattern, but a mirror azimuthal orientation for the tetra-anion and hence a mirror orientation for the tetramer (further detail in the SM, Fig. S2).

Density Functional Theory was used to model the system shedding light on the structure of the resulting metal-organic network. Starting from the observed 4×4 structure, we carried out structural relaxations on unit cells with different THQ:Cu (adatom) ratios (see SM, Fig. S3), in order to determine which

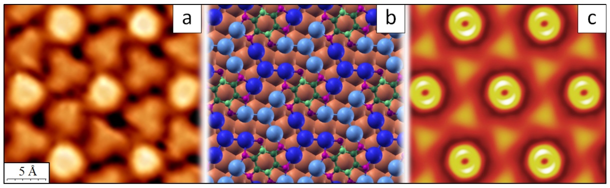

FIG. 2. (a) High-resolution STM image (bias = 0.55 V; I = 37.2 nA) of the THQ tetra-anions assembled on the Cu(111) surface; (b) corresponding DFT calculated structure, and (c) simulated STM image at 0.55 V obtained by using the Tersoff-Hammann approach[27] of the metal-organic network formed by TOQ tetra-anions on Cu(111) after an annealing to ∼385 K. Cu adatoms are represented as light and dark blue spheres in (b) for a better visualization of the copper tetramers, while TOQ-related atoms are colored according to XPS fitting (see below). The computed cell with parameter 10.22 Å is compatible with the experimental one observed by LEED and STM.

stoichiometry best matches the experimental STM images. Our analysis identified that the best ratio to be THQ:Cu (adatom) = 1:8 (*i.e.*, one tetra-anion and two Cu tetramers per unit cell, see Fig. 2b and Fig. S4). In particular, the structure in Fig. 2b is predicted to be energetically significantly more stable than the ones in Figs. S4 and S3 (see SM), and is thus our "best" predicted structure based on theory alone. Its corresponding simulated STM image is provided in Fig. 2c

The agreement with the experimental STM image, reported in Fig. 2a, is very good, confirming that the triangular-shaped features observed by STM can be interpreted as tetrameric Cu clusters. The ball and stick model in Fig. 2b illustrates how the tetrameric Cu clusters are formed by three peripheral adatoms that bind to O atoms located in TOQ tetra-anion moieties and a central adatom that does not interact with the organic medium. While the average ∼2.10 Å Cu-O bonding distance is consistent with values previously reported in the literature,[28–30] we find that the assembly structure contains three distinct Cu-O bonds. Namely, two O atoms bound to opposite benzene ring C atoms bind to a single Cu tetramer adatom (calculated bond length: 2.10 Å), while each of the remaining four O atoms in the TOQ molecule establish two non-equivalent coordination bonds with Cu atoms from different tetramers (bond lengths: 2.06 Å and 2.15 Å, respectively).

Moreover, DFT calculations confirm that the tetra-anions adsorb parallel to the substrate (SM, Fig. S5), with the phenyl rings and the oxygen atoms laying 3.24 Å and 2.99 Å above the surface layer, respectively. All the adatoms constituting the tetramer unit are located at hollow surface layer sites in a geometry that alternates tetramers in hcp and fcc positions, the adsorption distance of the central adatom being slightly longer than that of the peripheral ones (2.05 Å *vs.* 1.99 Å, values close to the (111) planes spacing). Our DFT results provide further insights into the electronic charge redistribution within the 4×4 metal organic network. Bader charge analysis evidenced a substantial 2.68 e^- charge transfer from the metal surface to the TOQ tetra-anions within the resulting metal organic self-assembled adlayer. In particular, we find that each oxygen-bonded copper contributes ∼0.39 a.u. to the total charge transferred to the organic medium, while the adatoms located at the center of the tetramers are practically unperturbed by the metal-organic coordination. The emerging charge rearrangement was better pointed out by calculating the differential electron charge density $\Delta\rho$(r) (*i.e.*, the difference between the charge density of the total system and the ones of the isolated tetra-anion and substrate), calculated as $\Delta\rho(\mathbf{r}) = \rho_{int}(\mathbf{r})$ - $[\rho_{sub}(\mathbf{r})+\rho_{mol}(\mathbf{r})]$.

The $\Delta\rho(\mathbf{r})$ surface plot detailed in the Supplementary Material (Fig. S6) reveals that the peripheral Cu adatoms display electron density depletion around the Cu-O bonds and a corresponding charge accumulation on TOQ tetra-anions. While the density transferred to the tetra-anions appears to be evenly distributed over oxygens' p-states, the carbons' π-cloud electron density intake is not uniform. In fact, less density is accumulated in correspondence to the two equatorial C atoms belonging to singly coordinated carbonyls (which we will refer to as C[+]; C[-] will be used to indicate the remaining 4 C atoms). The general picture of two different O and C species emerging from the calculations will be useful to interpret the core-level photoemission spectroscopy results, which we next describe.

In order to confirm the dehydrogenation process of THQ molecules upon annealing, we performed high energy-resolution core-level XPS (HR-XPS) measurements (Fig. 3) on THQ molecules deposited on the Cu(111) surface, before and after annealing. The molecules adsorb intact onto Cu(111) held at room temperature. In fact the O 1s spectra display two peaks, as obtained by fitting the data with Voigt functions (lorentzian-gaussian lineshape, further detail in the SM), at 530.45 eV and 532.50 eV (Fig. 3a). The component at lower binding energy (BE) is associated to C=O oxygen, while the peak at higher BE is associated to C-O-H. Consistently, the C 1s core level of as-deposited THQ molecules shows two contributions at 285.55 eV and 285.30 eV, associated to C=H (lower BE) and C-O-H (higher BE) carbon, respectively, plus the corresponding shakeup peaks (Fig. 3b). Previous works using molecules similar to THQ deposited on Cu(111) and Au(111) found that at RT the C=O groups point toward the substrate, which is reflected in the low BE of the respective C 1s and O 1s peaks.[11,12] As expected from the molecular stoichiometry for intact THQ molecules, the intensities (peak areas) of the C=O/O-H related components are in a 1:2 ratio for both the O 1s and C 1s peaks, thus confirming the adsorption of intact molecules at RT.

Upon annealing up to ∼385 K, both the O 1s and C 1s core level peaks change drastically (Fig. 3c,d). More in detail, the O 1s O-H associated peak disappears almost completely, indicating that most of the THQ molecules undergo a surface-assisted dehydrogenation after annealing, where copper atoms have a crucial role in the activation of the dehydrogenation process. Two main components appear in the spectrum at 530.35 eV and 531.30 eV BE, with a residual small signal due to some unreacted molecules (Fig. 3c). Referring to the model shown in Fig. 2b, the peak at 530.35 eV corresponds to oxygen atoms bound to two copper adatoms, while the peak corresponding to oxygen atoms bound to one copper adatom appears at higher binding energy. This assignment is justified by the DFT model, suggesting that there are four oxygen

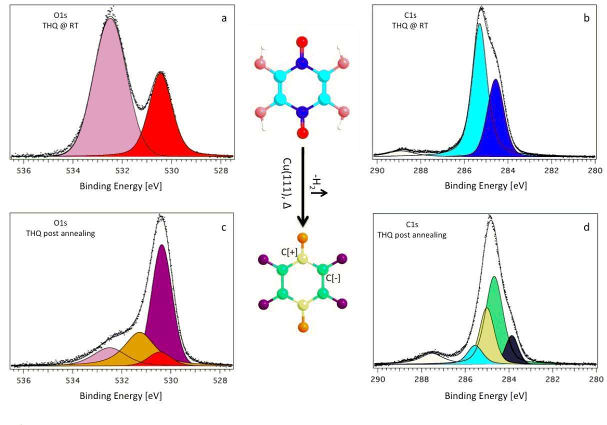

FIG. 3. O 1s (left) and C 1s (right) core level XPS measurements performed on (a,b) THQ molecules deposited on the Cu(111) surface at RT and (c,d) after an annealing up to ∼385 K, respectively; experimental data (dots) and results of a fitting analysis (continuous lines). The single fitting peaks are also shown and painted with the same colors of the corresponding atomic species reported in the central panel, where a sketch of the temperature-induced molecular reaction is reported.

atoms bound to two different copper adatoms and two oxygen atoms bound to one copper adatom only, fully consistent with the 2:1 intensity ratio in the XPS spectrum. After annealing, the C 1s peak is characterized by an intense component at 284.65 eV BE, associated to the C[-] atoms, and a second one, with an area equal to half of the first one, at 285.00 eV BE, corresponding to the two equatorial C[+] atoms. The C[-] atoms receive more charge from the substrate then the C[+]

atoms, which is reflected by the lower binding energy of the corresponding peak (Fig. 3d). The C 1s peak after the annealing is also characterized by a tail at low BE that can be explained by the presence of a low amount of graphitic carbon (black component at 283.90 eV) due to a partial degradation of the pristine intact molecules. It is worth to note that the TOQ synthesis has been possible only thanks to surface stabilization, as the high *ex-situ* reactivity of such organic tetra-anions prevents the possibility to directly sublimate them on the surface.

III. CONCLUSIONS

In conclusion, we synthesized and characterized a 2D-ordered assembly of interlinked copper tetramers through dehydrogenated THQ molecules on the Cu(111) surface. The ability to produce arrays of controlled spaced tetrameric Cu units is potentially very interesting for applications requiring size-selected ordered arrays of metal clusters. We fully characterized the as-deposited THQ molecules on Cu(111) and the post-annealing 2D metal-organic tetra-anion network. STM imaging and LEED patterns provided fundamental insights about self-assembling, while detailed XPS analysis provided information on the chemical state of the molecules and their adsorption configuration, and DFT calculations were crucial for revealing the presence of copper tetrameric clusters and interpreting the spectroscopic data. This led to a fully consistent characterization of the stable linkage structure of the tetrameric units within the metal-organic salt. The proposed method to obtain a 2D ordered array of copper tetrameric units embedded in an on-surface metal organic framework can open the perspective to apply this approach also to other molecular systems, by using ordered network of self-assembled pristine molecular units on surfaces, followed by gentle thermal procedures, so to be able to produce size-selected metal clusters of precise size and shape in a long-range ordered network.

IV. SUPPLEMENTARY MATERIAL

Additional STM images of single defects and chiral molecular assemblies; detail on the DFT calculation and on theoretical approaches towards optimisation of THQ and tetramer assembly; detail on the fitting procedures, are reported in the Supplementary Material file.

V. ACKNOWLEDGEMENTS

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