

Templated growth of an ordered array of organic bidimensional mesopores

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We report on a method to fabricate a porous two dimensional (2D) array of porphyrins on $c(2 \times 2)N/Cu(001)$ with pore sizes larger than 5 nm, larger than the reported sizes for hydrogen-bonded or coordination porous organic networks. When deposited on the square nanopattern created by partial nitridation of the Cu(001) surface, the porphyrin molecules prefer to adsorb on clean copper instead of adsorbing on the CuN islands, forming a porous 2D array. This nanopatterning technique can be straightforwardly extended to other molecular species to form the pore walls since its working principle only depends marginally on the nature of the intermolecular interactions. © 2008 American Institute of Physics. [DOI: 10.1063/1.2938702]

Porous materials are attracting wide interest because of the presence of cavities, which can host foreign molecular species for applications in filtering (molecular sieves) or chemical transformation (catalysts).¹⁻³ In either case, a high level of homogeneity in the pore size, shape, and chemical composition is required.¹ Whereas this is easily achieved for pore sizes below 2 nm in zeolites or open metallo-organic scaffolds, it is not straightforward to fabricate a material with a regular array of pores with characteristic dimensions larger than 2 nm.² In bulk, the first reported method to fabricate mesoporous materials used a liquid crystal as a surfactant,⁴ which acts as a template for the growth of silicates, leaving pores with sizes between 1.6 and 10 nm.

More recently, investigations about the adsorption and self-assembly of organic molecules on solid surfaces has led to the identification of two dimensional (2D) hydrogen-bonded^{5,6} and organometallic coordination networks^{7,8} with 2D pore sizes ranging from 0.5 to 2 nm, which determines the size of the molecules (e.g., the C₆₀ cluster size⁷) that the pores can accommodate. However, and with a few exceptions,^{6,8} the lateral size of a pore in a 2D molecular arrangement is related to the size of the constituent molecules. One would conclude that the use of larger and larger molecules would be the path to follow for the creation of larger pore-size networks, were it not because lateral van der Waals interactions, increasingly important for larger molecules, tend to produce close-packed structures instead of open molecular networks.

Inspired by the templating solution found to work for the fabrication of bulk mesoporous silicate materials, as well as a number of previous reports on the growth of one dimensional molecular structures on nanopatterned surfaces,⁹ we used the 2D nanopattern obtained by partial nitridation of the Cu(001) surface¹⁰ to steer the subsequent growth of porphyrin derivatives. The nitridation method (see below) leads to the creation of an ordered array of $c(2 \times 2)N-Cu(001)$ square islands, separated by bare Cu stripes a distance that can be modified at will by a careful control of the nitridation

conditions.¹¹ Subsequent porphyrin deposition leads to the selective adsorption of the molecular species on the bare Cu stripes, leaving the $c(2 \times 2)N$ areas uncovered, which thus become mesopores of the molecular network with regular sizes in the range of 5 nm.

The experiments were carried out in an ultrahigh vacuum chamber (base pressure of 10^{-10} mbar) equipped with a variable temperature scanning tunneling microscope (STM) and a rear-view four-grid low energy electron diffraction (LEED) optics, which was also used for Auger electron spectroscopy. The Cu(001) surface was prepared by cycles of Ar⁺ sputtering (500 eV) and annealing at 850 K. The flux of atomic nitrogen was obtained from a radio-frequency (rf) plasma source¹² operating with pure nitrogen gas at a pressure of 10^{-2} mbar. Meso-tetrakis(2,4,6 trimethyl)phenyl porphyrins (TMP) (see the inset in Fig. 1) were deposited on the clean copper surface, at room temperature, by thermal sublimation. STM measurements were performed at 150 K.

After the evaporation of 0.9 ML of porphyrins on the pristine Cu(001) surface (see Fig. 1), we can distinguish or-

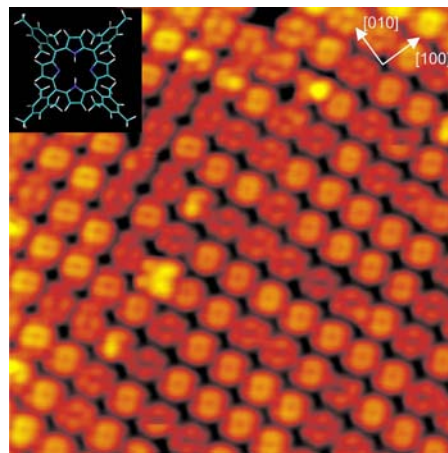


FIG. 1. (Color online) 20×20 nm² STM image of a Cu(001) surface after the evaporation of 0.9 ML of TMP. Inset: equilibrium configuration of an isolated TMP molecule in the gas phase (Ref. 13) (calculated by using the PM3 method from the HYPERCHEM 7.5 software).

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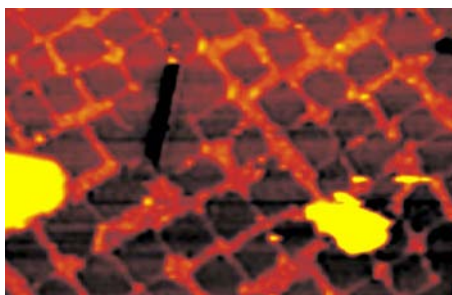


FIG. 2. (Color online) $53 \times 34 \text{ nm}^2$ STM image of a Cu(001) surface after the evaporation of 0.4 ML of atomic nitrogen and subsequent annealing at 600 K for 10 min. The surface displays a nanopattern of dark square nitrogen islands (5 nm size) separated by clean bright copper lines.

dered domains of molecules on the surface with a square unit cell of $\sim 1.64 \text{ nm}$. In these domains, two types of molecules, corresponding to two different conformations of the TMP molecule, are visible. One conformation (type I, the darker one) shows a rectangular appearance, with six lobes and two perpendicular mirror symmetry axes parallel to the high symmetry directions of the surface, resulting in two possible orientations of the molecules with respect to the substrate. This conformation can be interpreted as corresponding to the porphyrin lying flat on the surface. Due to the rotation of the mesityl groups around the σ bond, four methyl groups (one in each mesityl group) are above the average porphyrin plane (and are imaged as the four external lobes), while the porphyrin core adopts a saddle shape, which makes two of the pyrrole groups (the two internal lobes) higher than the other two.¹³ The second conformation (type II), which is never observed for isolated molecules, shows a slightly higher porphyrin core. We note that the tendency of this molecule is, thus, to form close-packed arrangements rather than open molecular networks due to the lack of groups capable of forming directional bonds (such as hydrogen bonds or coordination bonds) in the molecular periphery.

In order to create a mesoporous network out of this molecular species, we have nanostructured the copper surface by a partial nitridation: the adsorption of 0.4 ML of atomic nitrogen on a clean Cu(001) surface held at room temperature and subsequent heating at 600 K for 10 min produce a nanopattern of square islands with a dark appearance in the STM images (5 nm size), separated by bright lines that run parallel to the close-packed directions of Cu(100) (see Fig. 2). The dark islands contain a nitrogen $c(2 \times 2)$ superstructure, similar to copper nitride, and the bright lines are identified as clean copper.¹⁰ This nanopattern has been used as a template for growing metal nanostructures, such as nanodots of Co,¹⁴ Ni,¹⁵ and Fe¹⁶ on the intersections of the clean copper lines or rows of Ag,¹⁴ Fe,¹⁷ and Co¹⁴ on top of the clean copper lines.

After the evaporation of a very small amount of TMP on the $c(2 \times 2)\text{N}-\text{Cu}(001)$ nanopattern, the molecules display only the type I conformation, with a six-lobe appearance and the same two different orientations as in the pristine Cu(100) surface [Fig. 3(a)]. Moreover, they preferentially adsorb on the clean copper intersections, which reveals that the interaction with Cu is stronger than with the N-covered patches. At a coverage of 0.16 ML [Fig. 3(b)], TMP molecules cover the clean copper lines, forming short molecular wires, but they never adsorb on the nitrogen islands. For this coverage, there are also small deviations of the orientation of some

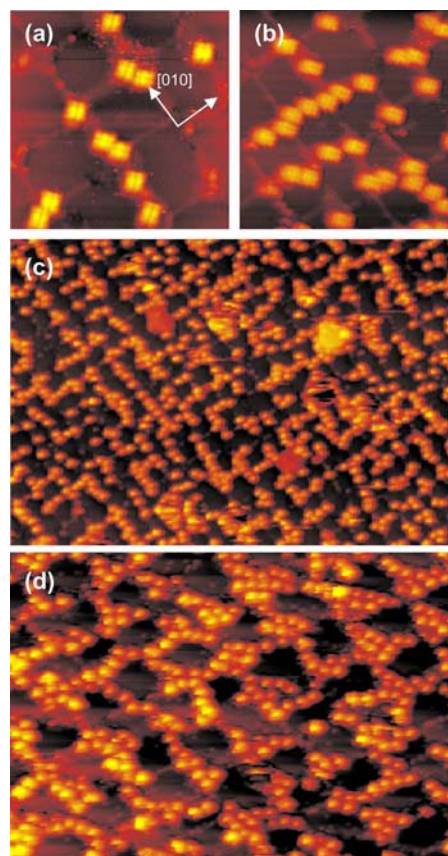


FIG. 3. (Color online) STM images of a $c(2 \times 2)\text{N}/\text{Cu}(001)$ surface after the evaporation of TMP. (a) $20 \times 20 \text{ nm}^2$, 0.07 ML of TMP. (b) $25 \times 25 \text{ nm}^2$, 0.16 ML of TMP. (c) $128 \times 75 \text{ nm}^2$, 0.30 ML of TMP. (d) $42 \times 79 \text{ nm}^2$, 0.43 ML of TMP. Upon increasing the coverage, porphyrins decorate completely the clean copper lines, developing a nanoporous molecular network of 4–5 nm porous sizes.

molecules, both on the intersections and on the copper lines, from the main symmetry directions of the surface. Increasing the amount of evaporated molecules to 0.30 ML [Fig. 3(c)] results in longer molecular wires, without adsorbing on the nitrogen islands. Finally, after the deposition of 0.43 ML on the $c(2 \times 2)\text{N}-\text{Cu}(001)$ nanopattern [Fig. 3(d)], we observe that the width of the molecular lines increases, starting to invade the nitrogen islands and thus distorting the square nanostructured surface pattern, but resulting in a porous molecular network with a pore size ranging between 4 and 5 nm.

The observed preference of some metals to adsorb in the clean copper areas has been alternatively ascribed to the passivation of the island region due to the Cu–N bonds,¹⁸ the difference in interfacial energy between the metal and the clean and $c(2 \times 2)\text{-N}$ areas,¹⁵ or to a combination of strain effects with inhomogeneities in the diffusion and/or the sticking process.^{16,19} In the case of the porphyrins, where molecule-substrate interaction is expected to be mediated by van der Waals forces, the porphyrin preference for copper results from stronger van der Waals forces between copper and porphyrin than between copper nitride and porphyrin due to the formation of the Cu–N bonds, which have a strong covalent character and hence decrease the polarizability.^{9,20} This is supported by the prediction that the adsorption energy of porphyrin derivatives on metals is larger than that on insulators.²¹ On the other hand, we believe that TMP prefers to adsorb initially on intersections just because it has plenty

of space there to adsorb on copper, so van der Waals forces are stronger than on the copper lines, where some parts of the molecule are floating over the edges of the nitrogen-covered patches.

In summary, we describe a nanoporous porphyrin network created by depositing porphyrins on a previously nanostructured metallic substrate and exploiting preferential molecule-metal interactions. This procedure could be also be useful for other molecular systems since it does not rely on the details of intermolecular interactions. Moreover, the larger mesopore size is interesting for trapping large molecules like small proteins, which could facilitate the development of applications in catalysis, biocompatibility, or organic electronics.

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