Boron Nitride Nanomesh: Functionality from a Corrugated Monolayer

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The decomposition of borazine $(HBNH)_3$ precursor molecules on the hot rhodium (111) surface leads to the spontaneous formation of a highly regular hexagonal structure with a periodicity of 3.2 nm and with the appearance of a mesh with pores of about 2 nm in diameter: the so-called nanomesh [1]. This nanomesh is identified as a single, complete monolayer [2,3]. The 2 nm sized pores are formed by regions where the layer binds strongly to the underlying metal, while the regular network of mesh wires represents regions where the layer is not bonded to the substrate, resulting in a corrugation of about 0.5Å in the layer [2]. The nanomesh exhibits a remarkable thermal stability and chemical inertness: it is robust against immersion in water and electrolyte solution [3]. Moreover, it shows the functionality of a regular array of trapping potentials as it is demonstrated by the stable and site selective adsorption of different kinds of planar molecules as observed in scanning tunneling microscopy and ultraviolet photoelectron spectroscopy [3]. Depending on the size of the molecules and the molecular coverage, individual molecules or molecular assemblies are trapped in the pores.

Naphthalocyanine (Nc) molecules were vapor-deposited onto the nanomesh kept at room temperature. These planar molecules have a conjugated pi-electron system and their diameter of about 2 nm is comparable to the nanomesh pore size. The Nc molecules form a well-ordered array with the periodicity of the nanomesh pores (3.22 nm) as observed in STM images (Fig. 1A). High-resolution images reveal that individual Nc molecules are trapped inside the pores, indicating a highly site-selective adsorption. Increasing molecular coverage leads to the continuous filling of all the nanomesh pores. Molecule-substrate interactions are therefore dominating the adsorption behavior and intermolecular interactions are weak. This behavior is in contrast to Nc on flat graphite layers where the structure formation within the molecular layer is dominated by intermolecular interactions. A completely different pattern (almost quadratic) is observed in that case, with a much smaller periodicity of 1.7 nm [4]. Thus, the Nc molecules form an array of equally spaced and well-separated indvidual molecules on the nanomesh [3].

The selective adsorption into the pores is also reflected in the normal emission UPS spectra (Fig. 1B). The spectrum of the clean *h*-BN layer on Rh(111) shows the appearance of two pairs of BN-related peaks and indicates the presence of two species of *h*-BN that have their binding energies for the σ and π band shifted by about 1 eV. Adsorption of the molecules on the nanomesh leads to an attenuation of the intensity of the σ_β component, whereas the other one (σ_α) remains unchanged for coverages up to one monolayer [5] (Fig. 1B). The σ_β component is associated to the nanomesh pores and the selective attenuation thus represents the trapping of the Nc molecules in the pores. Further increasing the coverage leads also to attenuation of the σ_α component that is related to the mesh wires.

In summary, the nanomesh paves the way for applications as a template for the growth of ordered nanostructures, based on methods that rely on ultrahigh vacuum deposition techniques as well as on deposition from aqueous solutions.

References:

[1] M. Corso et al., Science **303** (2004) 217.
[2] R. Laskowski et al., Phys. Rev. Lett. **98** (2007) 106802.
[3] S. Berner, M. Corso et al., Angew. Chem. Int. Ed. (2007), in press.
[4] M. Lackinger et al., J. Phys. Chem. B **108** (2004) 2279.
[5] The term monolayer refers in this case to one molecule per nanomesh pore.

Figures:

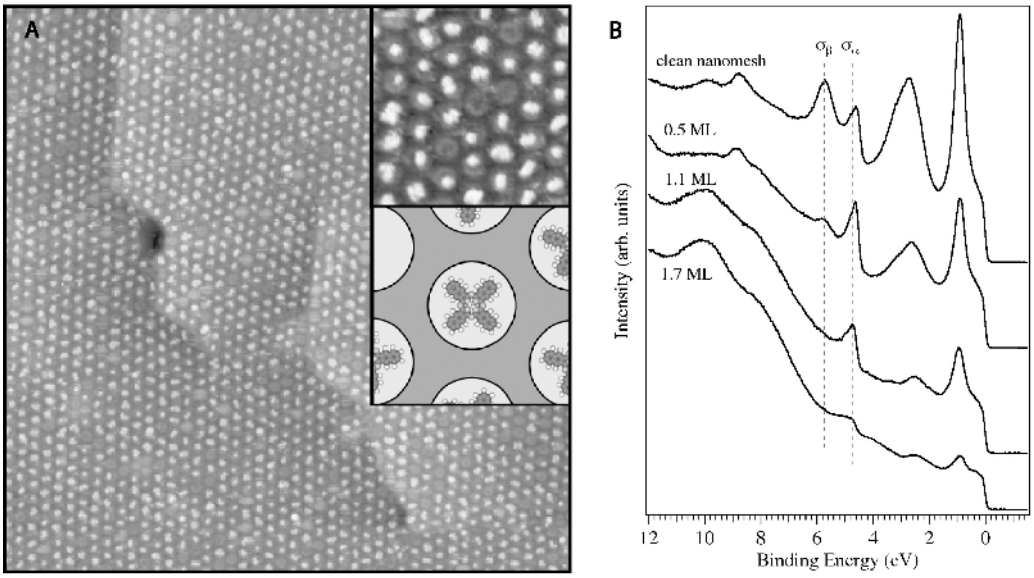

Figure 1: *Site-selective adsorption of naphthalocyanine ($C_{48}H_{26}N_{8}$) molecules in the nanomesh pores. A) STM image (120 nm x 120 nm, I = 0.3 nA, U = 1.3 V) showing a nearly complete monolayer [5] of Nc molecules on the nanomesh. The inset on the top right shows an enlargement (19 nm x 19 nm) and gives a high-resolution view that shows the trapping of the Nc molecules inside the nanomesh pores. The inset on the right shows a schematic representation of the molecular structure of naphthalocyanine (Nc) plotted on top of a nanomesh pore. B) Normal emission UPS spectra for increasing Nc coverage on the nanomesh. The site-selective adsorption of the Nc is reflected in the selective attenuation up to the first monolayer [5] of the σ_β component that is associated with the nanomesh pores. Further increasing the coverage leads also to attenuation of the σ_α component that is related to the mesh wires.*