Copper Phthalocyanine Molecular Arrays on SiC Nanomesh

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[Introduction]

To realize operational single molecular devices on a large scale, one promising approach is to assemble these functional molecules into well-ordered arrays. An appealing route to fabricate such molecular arrays is the self-assembly of molecules on surface templates that are naturally or artificially patterned at the nanoscale. Several approaches have been used to prepare nanotemplates, including surface reconstructions, surface modification via other molecules, and vicinal surfaces. However, the search for relatively simple methods to fabricate large highly ordered molecular arrays with adjacent single molecules separated from each other by a few nanometers is still challenging. Here we demonstrate a simple method to self-assemble copper phthalocyanine (CuPc) molecules into a highly ordered molecular array with flat-lying geometry on a nanomesh template, the so-called "silicon carbide (SiC) nanomesh"[1].

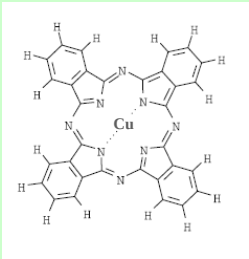
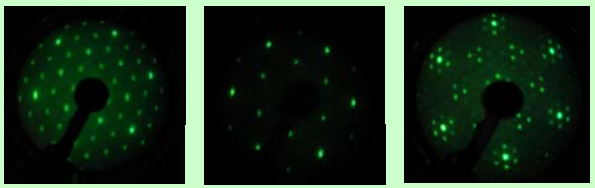


Fig 1 the molecular structure of Copper Phthalocyanine (CuPC)

CuPC is a common molecule which has good chemical and thermal stability and outstanding electronic properties. It has been widely applied in gas sensor, organic thin-film transistors, organic light-emitting diodes and solar cell. Here we utilize the planar geometry of CuPC molecule as a model molecule to enhance the molecule-substrate interaction in favor of templated growth.



a) b) c)

Fig 2 LEED pattern of 6H-SiC (0001) reconstructed surface.
a) 3×3, b)$\sqrt{3}\times\sqrt{3}$ R30°, c)$\sqrt{6}\times\sqrt{6}$ R30°

In the evolvement of 6H-SiC(0001) surface by annealing accompanied by silicon source, there are three important reconstructions (figure 2). The $6\sqrt{3}\times 6\sqrt{3}$ R30° has been demonstrated to be effective in isolating metal nanoclusters[2]. In this experiment we prove it is a good template to form CuPC molecular arrays.

[Experiment]

Experiments were carried out in a UHV chamber with a base pressure of 1×10^{-10} mbar at the ***SINS*** beamline[3] of ***Singapore Synchrotron Light Source***.

The SiC nanomesh surface was prepared by annealing a Si-terminated n-type 6H-SiC(0001) substrate (CREE research Inc.) at 1150 ºC for 30 minutes. CuPc (Sigma-Aldrich, sublimation grade) molecules were thermally evaporated onto the nanomesh surface by a Knudsen cell (MBE-Komponenten, Germany) at 380 ºC while the substrate was kept at room temperature. A low deposition rate of 1 monolayer (ML) per hour was used for controllability.

[Result and Discussion]

A. X-ray Photoelectron Spectra of CuPC on SiC nanomesh

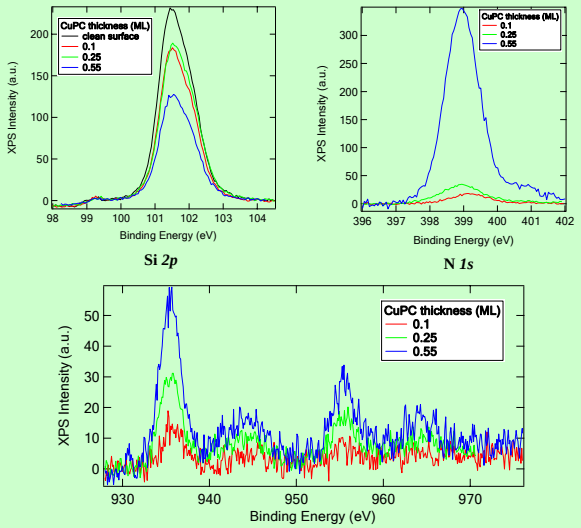


Figure 3 The decrease of Si *2p* peak while the increase of N *1s* peak and Cu *2p* peak indicated the growth of CuPC molecules

B. Near Edge X-ray Absorption Fine Structure (NEXAFS)

Using the intensity ratio between I(90º) and I(20º), we estimate the average orientation of CuPc molecular planes to be about 26º±5º with respect to the nanomesh surface. The observed flat-lying geometry of CuPc indicates that the interaction between CuPc and the underlying SiC nanomesh is essentially a π-π interaction.

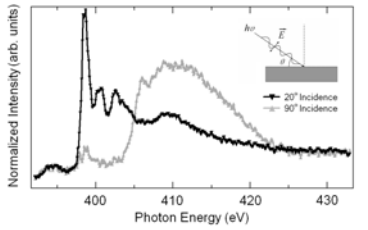


Figure 4 Nitrogen *K*-edge NEXAFS spectra for silicon carbide nanomesh surface with a nominal thickness of 0.5 monolayer of CuPc molecules measured at photon incidence angles of 20º (black curve) and normal incident angle (grey curve), respectively.

C. Scanning Tunneling Microscopy images

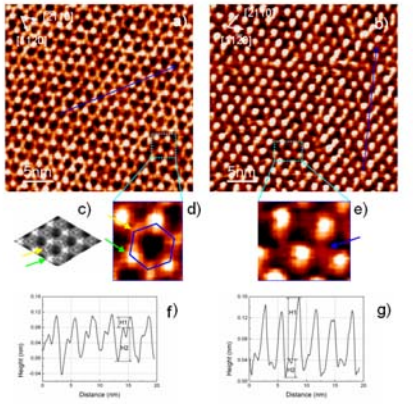


Fig5. 0.55ML CuPc molecules on SiC nanomesh surface. (a) STM image of clean nanomesh surface 30×30nm², VT=-2.1V, IT=0.38nA. (b) After CuPc growth 30×30nm² scan VT=-3.3V, IT=39pA. (c) Calculated STM image of nanomesh surface (copied with permission from ref.(1). (d) and (e) are the STM images zooming from (a) and (b) respectively. The blue hexagon in (d) is the unit cell of nanomesh as well as the white hexagon in (c). The blue arrow highlights the underlying structure of substrate. (f) and (g) are the corresponding depth profiles along the blue lines in (a) and (b) respectively. The green and yellow arrows indicate the bright vertex and dull vertex in the experimental (a) and the calculated (c) STM images respectively.

It has been observed that CuPc molecules grown on many atomically flat substrates such as highly oriented pyrolytic graphite (HOPG) and Ag(111) aggregate into four-fold symmetric crystalline islands. Here we demonstrate the first three-fold symmetric CuPc molecular array induced by underlying honeycomb-like nanomesh substrate.

[Conclusion]

- **Highly-ordered molecular arrays with three-folder symmetry have been self-assembled by the deposition of CuPc on the SiC nanomesh.**
- **Angle-dependent NEXAFS measurements reveal that CuPc molecules lie flat on the surface.**
- **The ultra-high surface density as well as periodicity of this molecular array provides possibilities for molecular electronics and nanotechnology.**

1. W. Chen, H. Xu, L. Liu, X. Gao, D. Qi, G. Peng, S.C. Tan, Y. Feng, K.P. Loh, and A.T.S. Wee, *Surf. Sci.* **596**, 176 (2005).
2. W. Chen, K.P. Loh, H. Xu, and A.T.S. Wee, *Appl. Phys. Lett.* **84**, 281 (2004).
3. X. J. Yu, O. Wilhelmi, H. O. Moser, S. V. Vidyarai, X. Y. Gao, A. T. S. Wee, T. Nyunt, H. Qian, and H. Zheng, *J. Electron Spectrosc. Relat. Phenom.* **144–147**, 1031 (2005)