Evaporation driven particle packing has been investigated to reveal interesting patterns at micrometer to millimeter scale. While the microscopic structures of these patterns are well characterized, the molecular level arrangements of individual molecule or particle in these patterns are less known mainly due to the difficulties in attaining high-resolution images. Additionally, as the line tension at the ring front could impact assembly or packing, the validity of this effect at the nanometer and molecular level still needs to be confirmed. This work uses scanning tunneling microscopy (STM) for the investigation of the packing of G4-polyamidoamine (PAMAM) dendrimers on gold substrates at meso and nanometer scales, upon solvent evaporation. Dendrimers were pre-coordinated with Pt$^{2+}$ ions to increase conductivity to enable STM imaging. Novel patterns are revealed at the nano- to mesoscopic level: e.g. near periodic line arrays with craters decorating the lines and polymorphic line gratings. The monolayer deep craters range from 20 to 80 nm in diameter. The spacing of the lines measures from 5 to 10 nm. This work demonstrates that novel nano-patterns are induced by evaporation driven effect, and that STM provides the means for investigating the nano and mesoscopic nanomaterial assembly by line tension.
“Coffee Ring” Effect and Marangoni Flow

- During solution evaporation, there are two major competing evaporation-driven effects, “coffee ring” effect and Marangoni flow.

**“Coffee ring” Effect**

- Dense, ring-like structure along the perimeter
- 1) Absence of circulating flow
- 2) Contact line of drying droplet is pinned
- 3) Outward flow carries solutes to the periphery

**Marangoni Flow**

- Ordered structure across the surface
- The surface tension driven flow carries particles inward toward the top of the droplet and then plunges them downward where they can either adsorb onto the substrate near the center of the droplet or be carried along the substrate to the edge, where they are re-circulated along the free surface back toward the top of the droplet.

- In practice, Marangoni flow are introduced to suppress the “Coffee ring” effect in order to produce a well-ordered pattern.

Study Marangoni Flow at Nanoscale

- Current study of patterns induced by Marangoni flow are in the millimeter and micrometer scale, such as:

  - Concentric rings of anthracene with line spacing ranging from 600 nm to 100 μm
  - Arrays of pseudo parallel lines of dendrimers with periodicity of 550 nm

- However, nanofabrication method with nanoscopic precision control requires understanding the Marangoni flow at nanoscale.

- Our work investigates the Marangoni flow at the nanoscale, using dendrimer nanoparticles as readers.

  *Macromol Rapid Commun, 2015, 36(7), 616-20
  Nanoscale, 2011, 3, 1855*
STM is the highest spatial resolution imaging technique which can provide local electronic structure.
Imaging Dendrimers by High-Resolution STM

Sample Preparation of PAMAM Dendrimer for STM Imaging

ACS Nano, 2011, 5(3), 1685
Key Steps of Studying Marangoni Flow at the Nanoscale

(1) Pipette dendrimer aqueous solution onto Au substrate

(2) Droplet shrinkage by evaporation in N₂ stream

(3) N₂ stream

(4) Pattern revealed by STM imaging

Droplet divided into multiple nanodroplets

Particle pinned down as induced by Marangoni flow
Nano-patterns of G4-PAMAM-NH$_2$ induced by Maragoni flow were revealed by high-resolution STM.

The appearance of multiple domains indicates the transient drying region is divided into multiple drying domains of dimension less than 150 nm.

The coexistence of craters and parallel lines indicates that evaporation driven effect at the nanoscale present as dual motions, including hole expansion and “stick and slip” motion.
Arrays of Pseudo Parallel Lines with Single Molecular Width and Nanometer Spacing

- Line patterns were observed among dendrimers with different termini, such as amine, hydroxyl and PEG.
- Line spacing of the pattern ranges from 5 to 10 nm.
- Line patterns were formed due to “stick and slip” motion induced by Marangoni flow at the nanoscale. Nano-droplets with high contact angle formed during evaporation leads to sub-10 nanometer line spacing.
Nano-craters were of monolayer deep, with diameter ranging from 20 to 85 nm.

Raised edges of the nano-crater were revealed by AFM.

Possible mechanism for the crater can be explained by the “hole expansion mechanism” theory.

- When the thickness of the liquid thin film drops below critical thickness, holes are formed to restore the equilibrium film thickness.
- Hole opens, pushing out the particles along their contact line.
- Further packing of particles at the ring edge is induced by the inward flow of the solution.
- Particles will be stuck when the force cannot overcome the friction.


AFM nanoshaving reveals the thickness of dendrimer pattern is $2.2 \pm 0.3$ nm, which is consistent with the radius of dendrimer nanoparticle.
Conclusion

- Nanopatterns of dendrimer nanoparticles produced on Au(111) substrate were induced by evaporation of the nanoparticle aqueous solution droplet.
- Novel pattern of monolayer deep nano-craters with diameters ranging from 20 to 85 nm inlaid the single molecular width pseudo parallel lines with spacing ranging from 5 to 10 nm were observed.
- The formation of nano-droplets combining the Marangoni flow inside nano-droplets produced the sub-10 nm parallel lines.
- The formation of nano-crater structures were induced by evaporation driven force, which can be explained by the “hole expansion mechanism” theory.
- High resolution STM imaging resolved these nano-patterns of dendrimers with metal ion coordination.
Acknowledgement

- We thank Mr. Yang Liu and Dr. Jianli Zhao for many helpful discussions.
- The authors gratefully acknowledge the support from Gordon and Betty Moore Foundation, National Science Foundation and University of California, Davis.