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Tip-Patched Nanoprisms from Formation of Ligand Islands

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Background…

- Due to enthalpic preference, ligands tend to cover the less-coordinated curved tips.
- Simulations suggested that ligands attached to curved surface have more entropic gain than those on flat surface, which depends on the ligand length and structure.

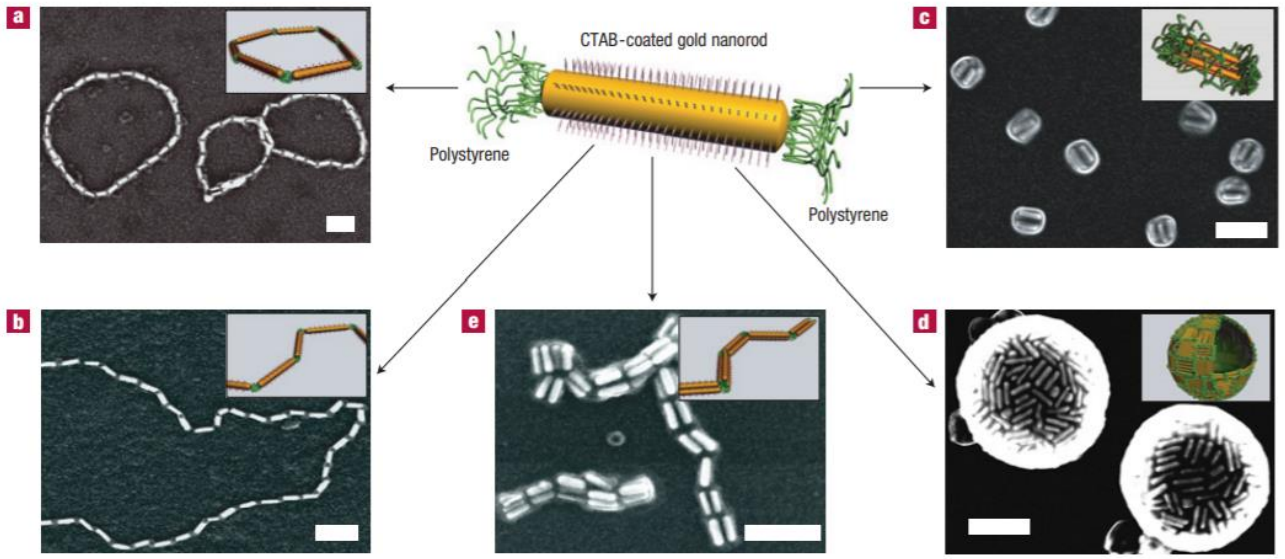
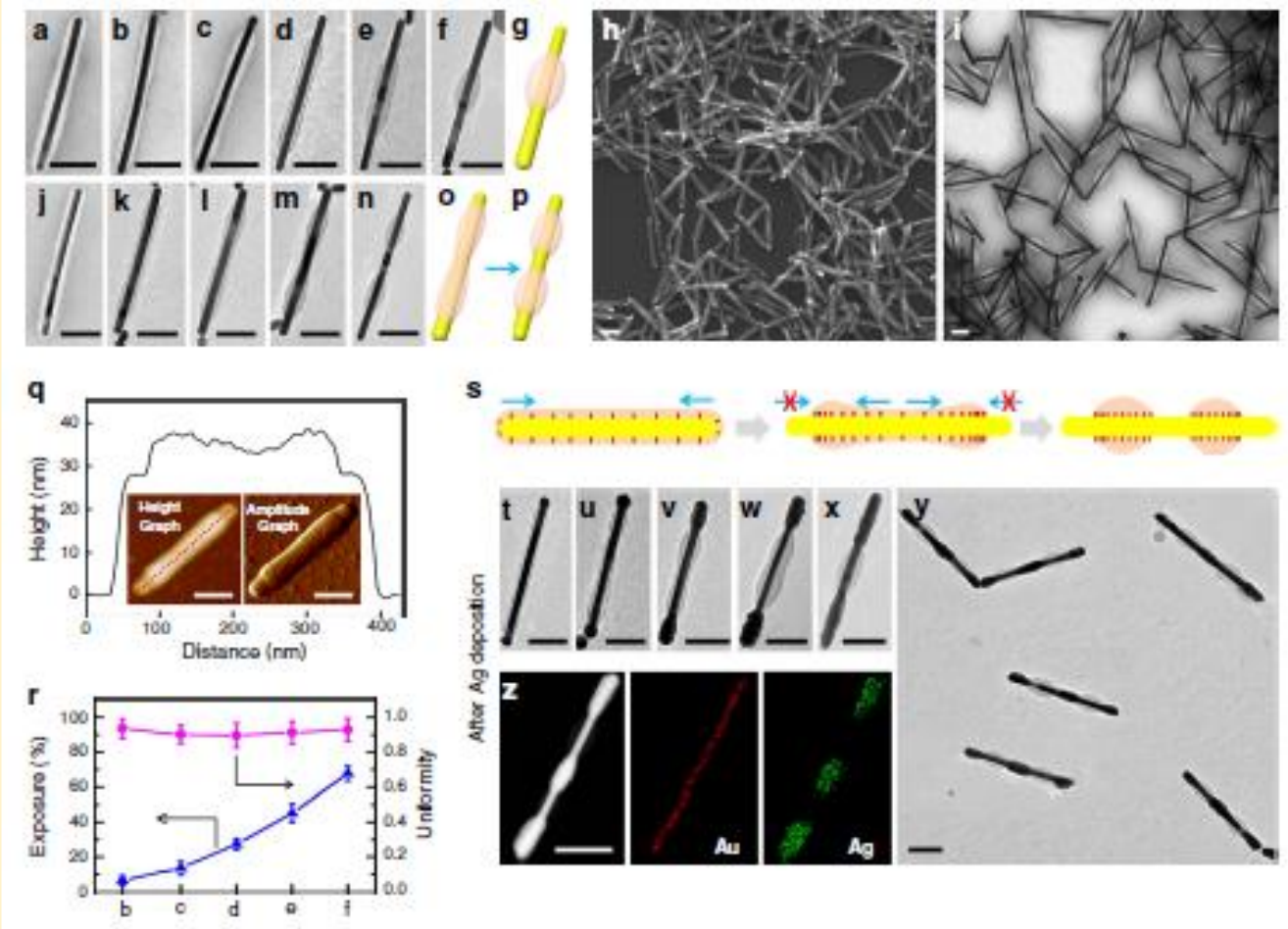


Figure 1 Self-assembly of polymer-tethered gold nanorods in selective solvents. An amphiphilic gold nanorod carrying a double layer of CTAB along the longitudinal side (the {100} facet) and polystyrene molecules grafted to both ends. **a**–**e**, SEM images of the self-assembled nanorod structures: rings (**a**) and chains (**b**) self-assembled in the dimethyl formamide/water mixture at water contents of 6 and 20 wt%, respectively, side-to-side aggregated bundles of nanorods (**c**) and nanospheres (**d**) self-organized in the tetrahydrofuran/water mixture at water contents of 6 and 20 wt%, respectively, and bundled nanorod chains obtained in the ternary dimethyl formamide/ tetrahydrofuran/water mixture at a weight ratio of liquids 42.5:42.5:15 (**e**). The scale bars are 100 nm. The insets show corresponding schematic diagrams of the nanorod assemblies.

Nat. Mater. **2007**, *6*, 609.

PS-b-PAA =Polystyrene-block-poly(acrylic acid)



Nat. Commun. **2018**, *9*, 563.

Introduction…

- "Island-like" ligand domains can be formed in self-assembled monolayers of thiolated molecules on planar gold substrates where ligand adsorption sites nucleate on the substrates, followed by lateral expansion of these sites into islands.

- This mechanism can pattern the NPs with precisely sized ligand islands, namely surface patches. These patchy NPs have great potentials in directed assembly, catalysis, and drug delivery.

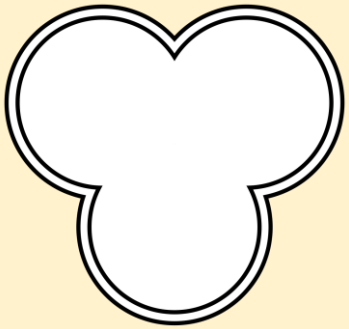
- One way is post-adsorption reorganization of uniformly coated polymer ligands on NPs upon a change in solvent polarity or temperature, but no control on patch sizes.

- Preferential ligand adsorption at the vertices or edges in gold tetrahedral and octahedral NPs are reported, although not realizing further extension into controlled patches.

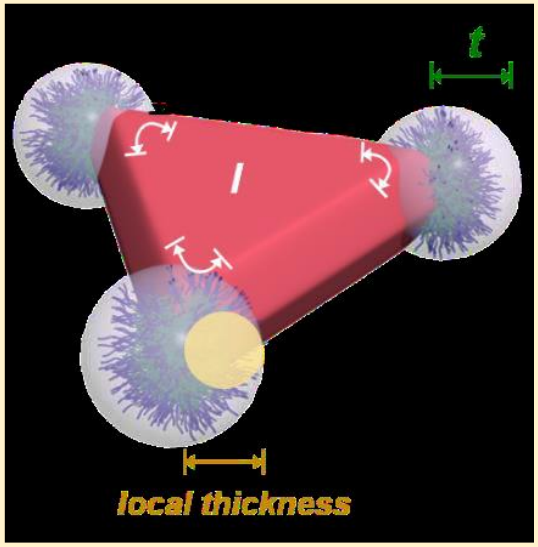
- Here is implemented the concept of ligand island formation for the first time to make patchy NPs with precise patch size and shape.

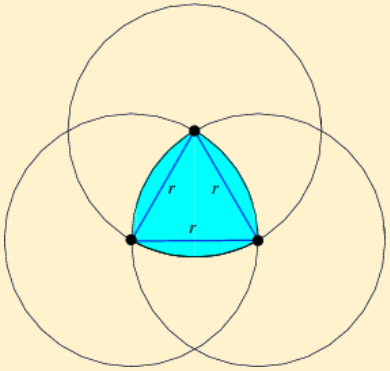
In this paper…

1. They apply the concept of "island formation" established for planar substrates, where ligands laterally cluster as they adsorb, to preparing nanoparticles (NPs) with precisely sized surface patches.
2. Preferential adsorption of 2-NAT on the prism tips leads to formation of tip patches. The patches are rendered visible for direct TEM and AFM imaging upon attaching polystyrene-b-poly(acrylic acid).
3. The shape of patchy prisms is varied from small lobed, big lobed, trefoil, T-shaped to a reuleaux triangle by increasing the 2-NAT-to prism concentration ratio.
4. This trend matches with predictions of island formation as elucidated by our self consistent field theory modeling, from which we exclude Langmuir adsorption.
5. The tip-patched prisms assemble into unexpected twisted dimers due to the patch–patch interactions.



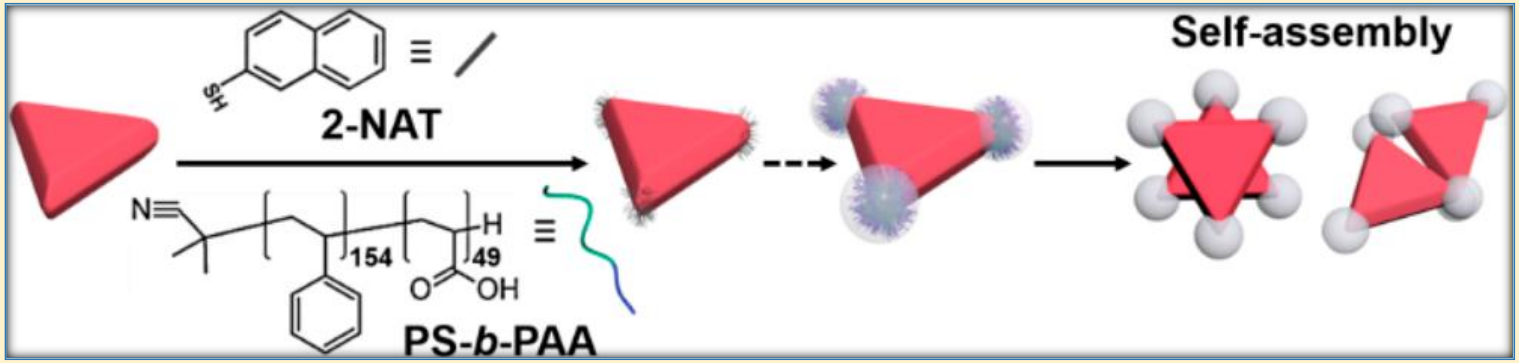
Trefoil triangle





Reuleaux triangle

The Scheme…



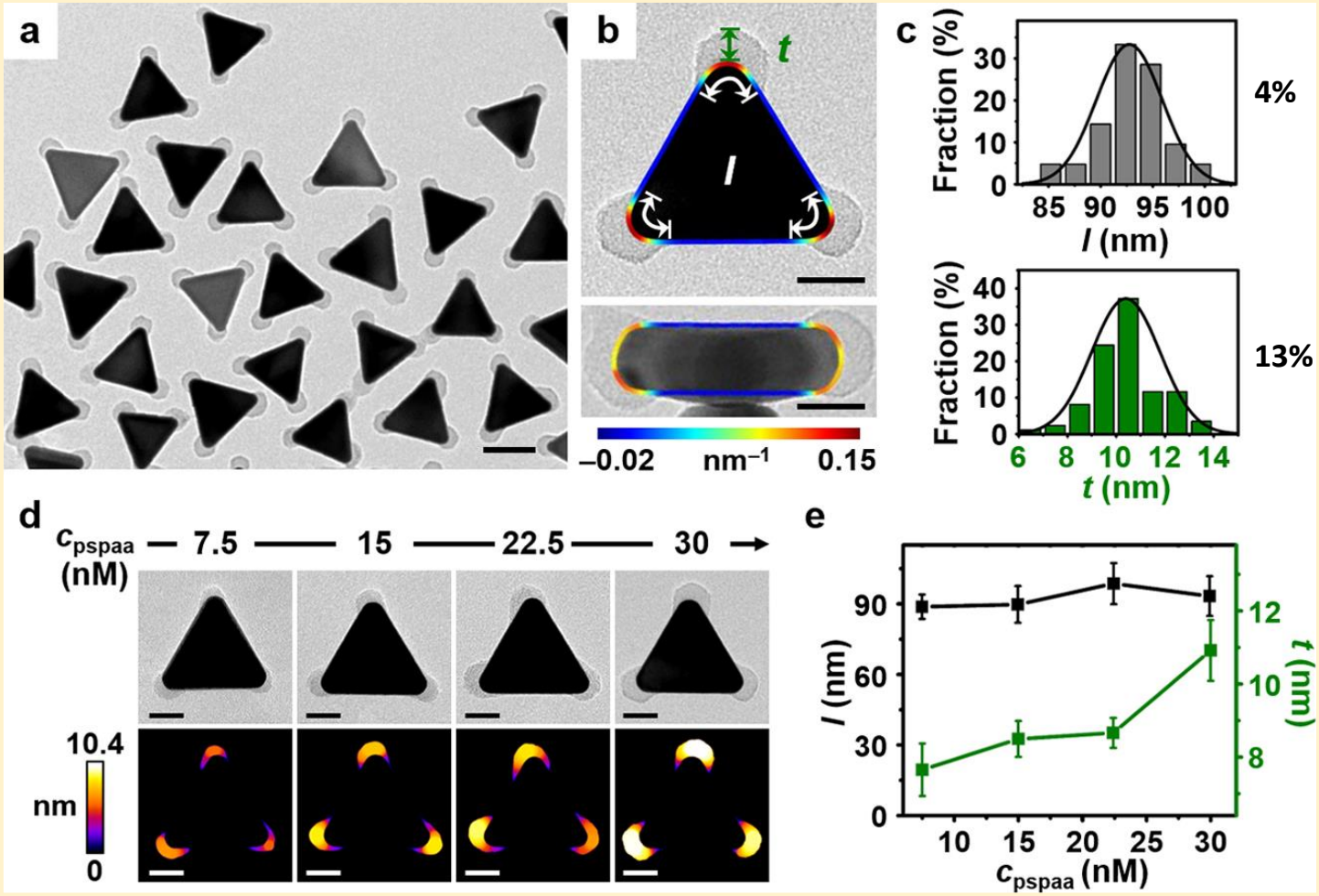
Scheme 1. Preparation of Tip-Patched Nanoprisms via Ligand Island Formation and Their Self-Assembly into Stars and Slanting Diamonds

What they did?

1. Synthesized gold prisms (58.9 ± 4.7 nm, 21.6 ± 1.8 nm).
2. It was mixed with 2-NAT and PS-b-PAA in a DMF/H_2O mixture at 110 °C for 2 h.
3. α = [2-NAT] : OD of the prisms at λmax, is 0.12 mM.

What happened?

1. Preferential adsorption of 2-NAT to curved tips over the planar faces.
2. Strong lateral π–π attraction of 2-NAT promotes the expansion of the initial adsorption sites into islands of desired sizes.
3. The hydrophobicity of 2-NAT allows polystyrene-b-poly(acrylic acid) (PS-b-PAA) to attach on the 2-NAT patches due to hydrophobic attraction.



Why?

Due to more extended conformation of PS-b-PAA as the packing density on the prism tips increases.

Figure 1. Tip-patched gold triangular nanoprisms. Low-magnification (a) and high-magnification (b) TEM images of tip-patched gold prisms, the latter overlaid with prism contours colored to local curvature, (c) Histograms of the cover length l and patch thickness t of the patchy prisms in panel a. (d) Representative TEM images (top) and local thickness analysis of patchy prisms as c_{pspaa} increases, at a constant α. (e) Plot showing how t and l change with c_{pspaa}. Scale bars: 50 nm (a), 20 nm (b,d).

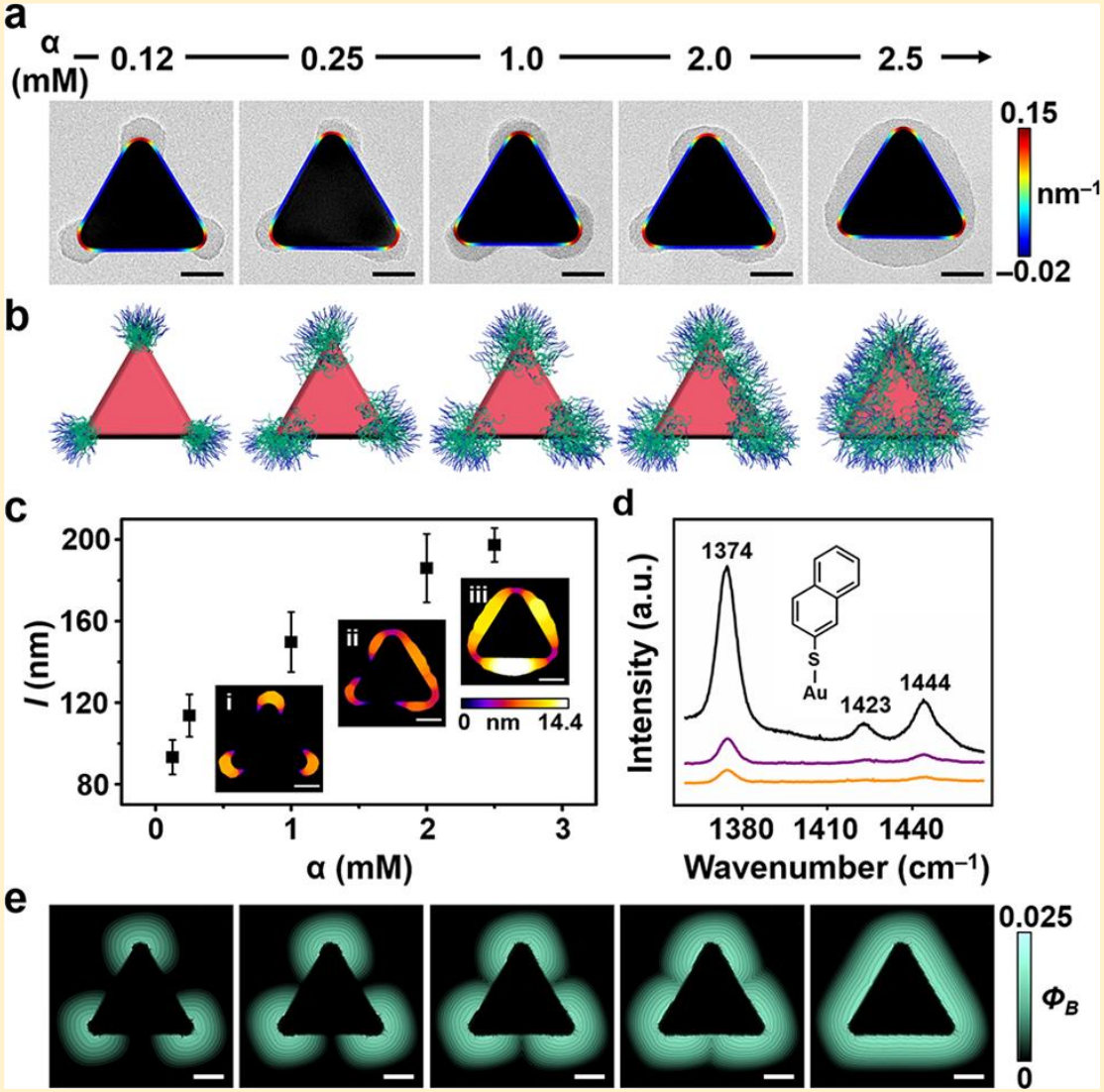


Figure 2. Surface patches from ligand island formation.
TEM images (a) and schematics (b) of patchy prisms synthesized at varying α. (c) Plot showing increased cover length l with increasing α. Inset:
local thickness maps of small lobed (i), T-shaped (ii), and reuleaux triangle (iii) patchy prisms. (d) Raman spectra of gold prisms at α = 0.12 mM (orange), α = 1.0 mM (purple), and α = 5.0 mM (black)

(e) Volume fraction maps of the charged B block, ϕ_B, for patchy prisms obtained from SCFT, where patches are formed from lateral expansion of ligand islands nucleated at the tips. The patch size Λ, is 3, 7, 12, 20, 40 from left to right. Scale bars: 20 nm (a,c,e).

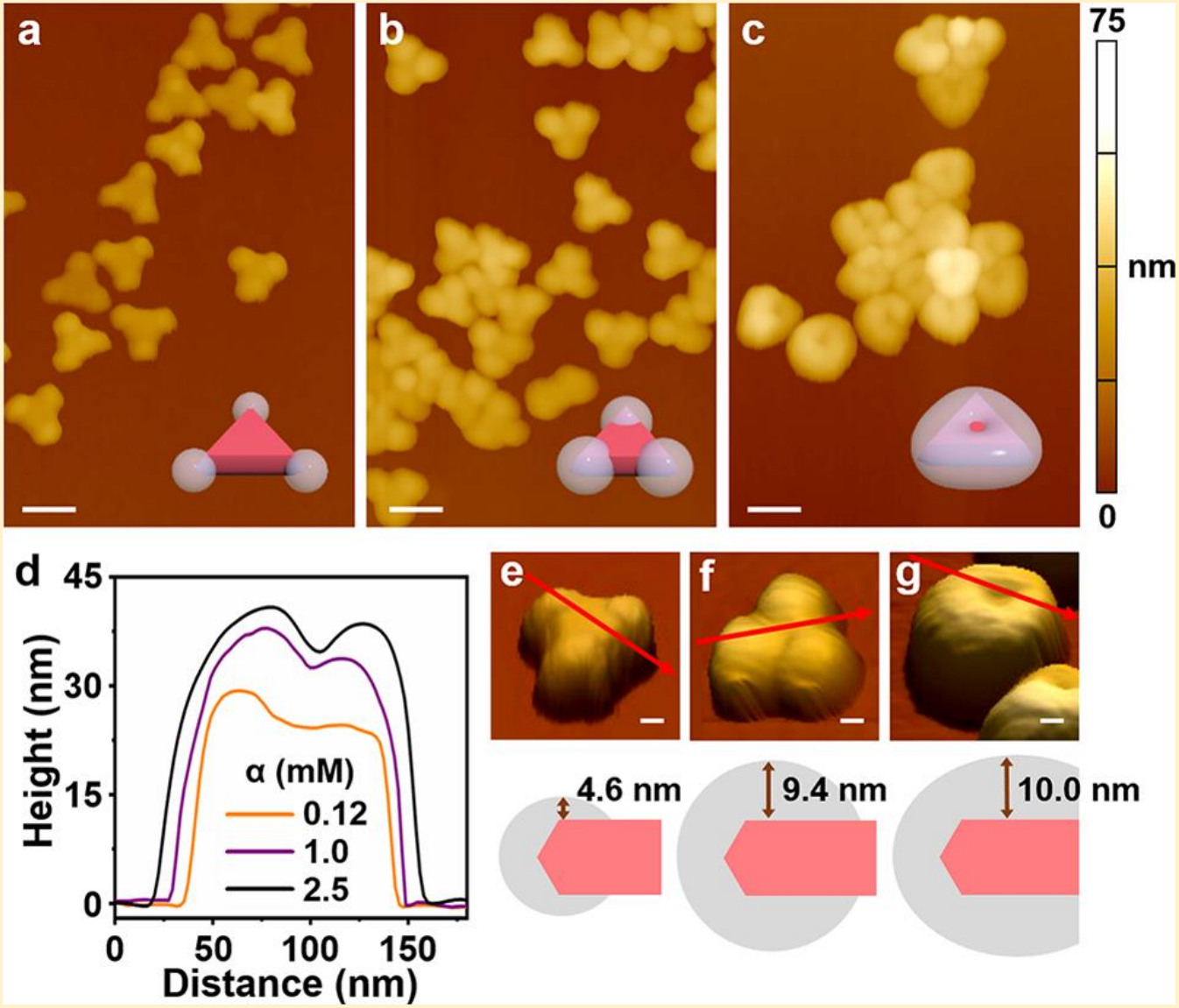


Figure 3. AFM analysis of 3D-shaped patches. (a−c) AFM images and schematics of small lobed, trefoil, and reuleaux triangle patchy prisms. (d) Height analysis on the patchy prisms based on line scans labeled in red arrows in the AFM images (top in e−g) and the corresponding side-view schematics (bottom in panels e−g). Scale bars: 100 nm (a−c), 20 nm (e−g).

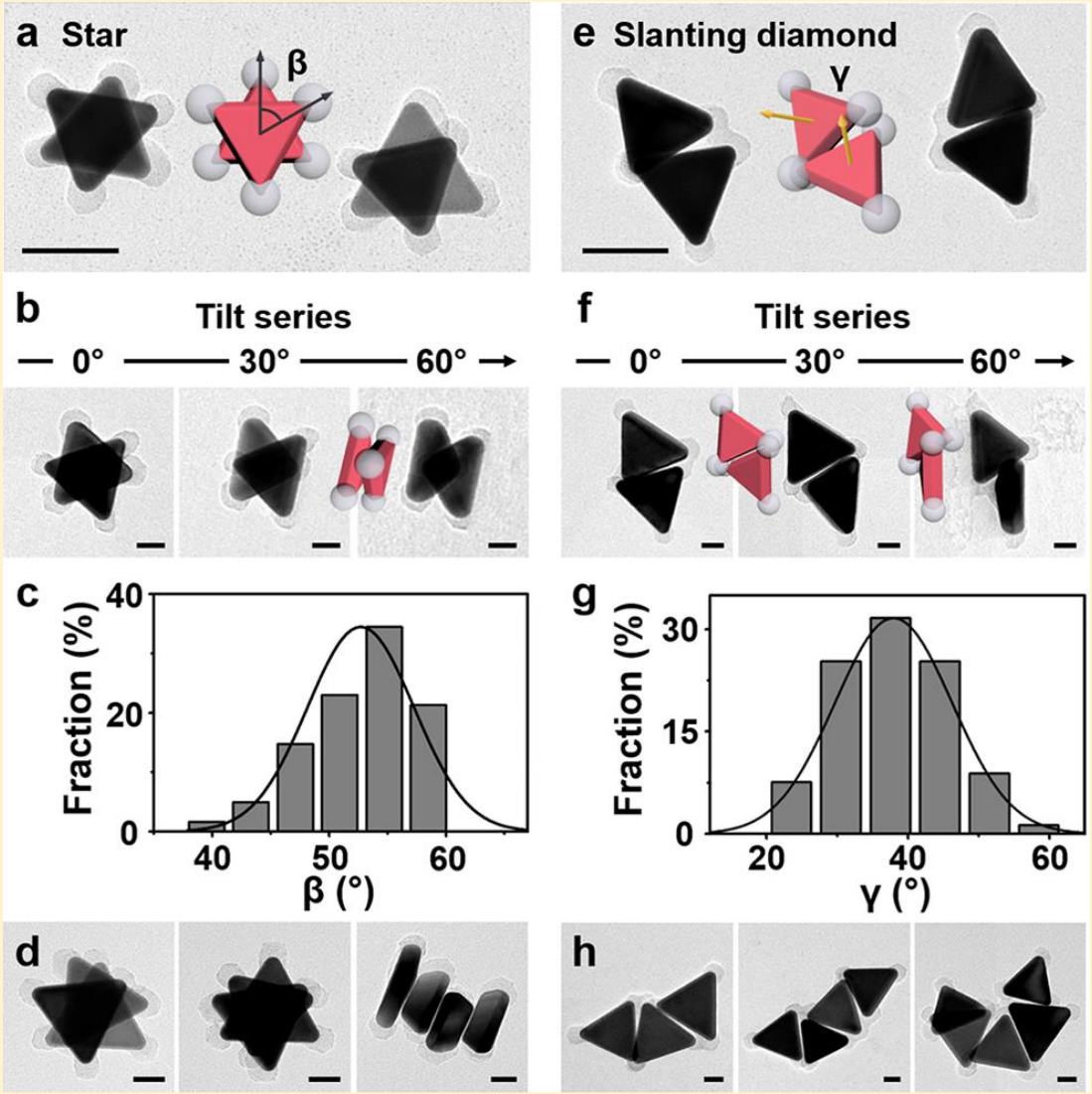


Figure 4. Self-assembly of small lobed prisms into twisted (a–d) star and (e–h) slanting diamond structures. (a,e) TEM images and schematics with angle notation, (b,f) TEM tilt series, (c,g) histogram of misaligned angles, and (d,h) TEM images of the assemblies. Scale bars: 50 nm (a,e), 20 nm (b,d,f,h).

When the ionic strength, I was increased to 66.7 mM, it screened the electrostatic repulsion
between PAA blocks.

Star : Faces together – on plane rotation – patches are distant - misalignment angle ß = 52.4°,no of trimers and tetramers are more at a higher I (80–100 mM).

Slanting diamond : Sides together – out of plane rotation – patches overlap – dihedral angle γ = 38.7 ± 8.3°

Slanting diamond is the preferred structure and its yield slightly increases at a higher I.


thank
you