POSTER #25

CONTROLLING THE SHAPE OF NANOPARTICLE SUPRACRYSTALS WITH SMALL MOLECULES

Kristina Kučanda, Johannes Ahrens, Michał Sawczyk, Sophia Buhbut-Sinai and Rafal Klajn

Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, Israel

Self-assembly of nanoparticles into polyhedral supracrystals is typically mediated by (bio)polymers (such as DNA) or charged ligands in polar solvents, mainly water [1]. However, nanoparticle assembly without macromolecules and in less polar solvents can be experimentally simpler, faster, and give different nanostructures and hybrid materials. Much less is known about interactions which govern such assembly than about aqueous systems. Magnetic nanoparticles are especially interesting because of the competition between different types of interactions [2].

Here, we mixed quasi-spherical gold (around 6 nm in diameter) or magnetite (around 9 nm) nanoparticles with small molecules which can interact with their surfaces. The mixture crystallized from toluene by exposure to vapor of a more polar non-solvent such as methanol for a few hours to days (gas-phase destabilization method) [3]. The precipitate was drop-cast on a silicon wafer, washed with methanol, and imaged with scanning electron microscope (SEM Ultra 55 FEG, Zeiss, at 8 kV), which revealed micrometer-sized supracrystals of clearly resolved, usually very regularly closely packed nanoparticles (Figure 1).

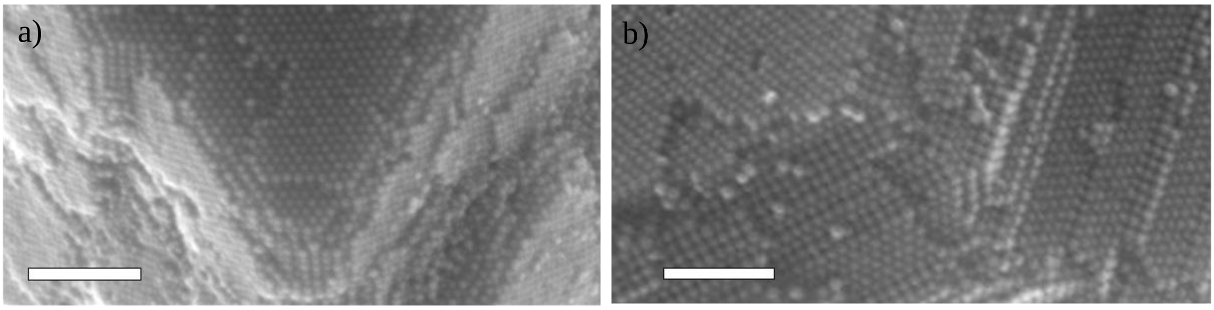

Figure 1. Supracrystalline arrangement of nanoparticles around a vertex of a) gold octahedron and b) magnetite hexagonal plate. SEM images, scale bars = 100 nm.

Different non-solvents and additives resulted in supracrystals of different shapes. The samples had pronounced selectivity for one or two types of shapes each. By the amount and type of additive gold assemblies could be tuned between spheres, spherically blunted octahedra, octahedra, and octahedra with protrusions (Figure 2a, c, d), and by different non-solvent into porous forms (Figure 2b). Magnetite assemblies could be made with spherical, hexagonal and pentagonal symmetry depending on the type of the additive (Figure 2e, f); and as long wires with the corresponding cross-section by assembly in permanent magnetic field (Figure 2g).

The results can be explained by different affinity of binding molecules for different crystal planes of nanoparticles, which amplifies nanoparticle surface anisotropy. The insights into controlling shape of crystals and other nano- and microscale assemblies are important for bottom-up chemical synthesis of materials at all scales.

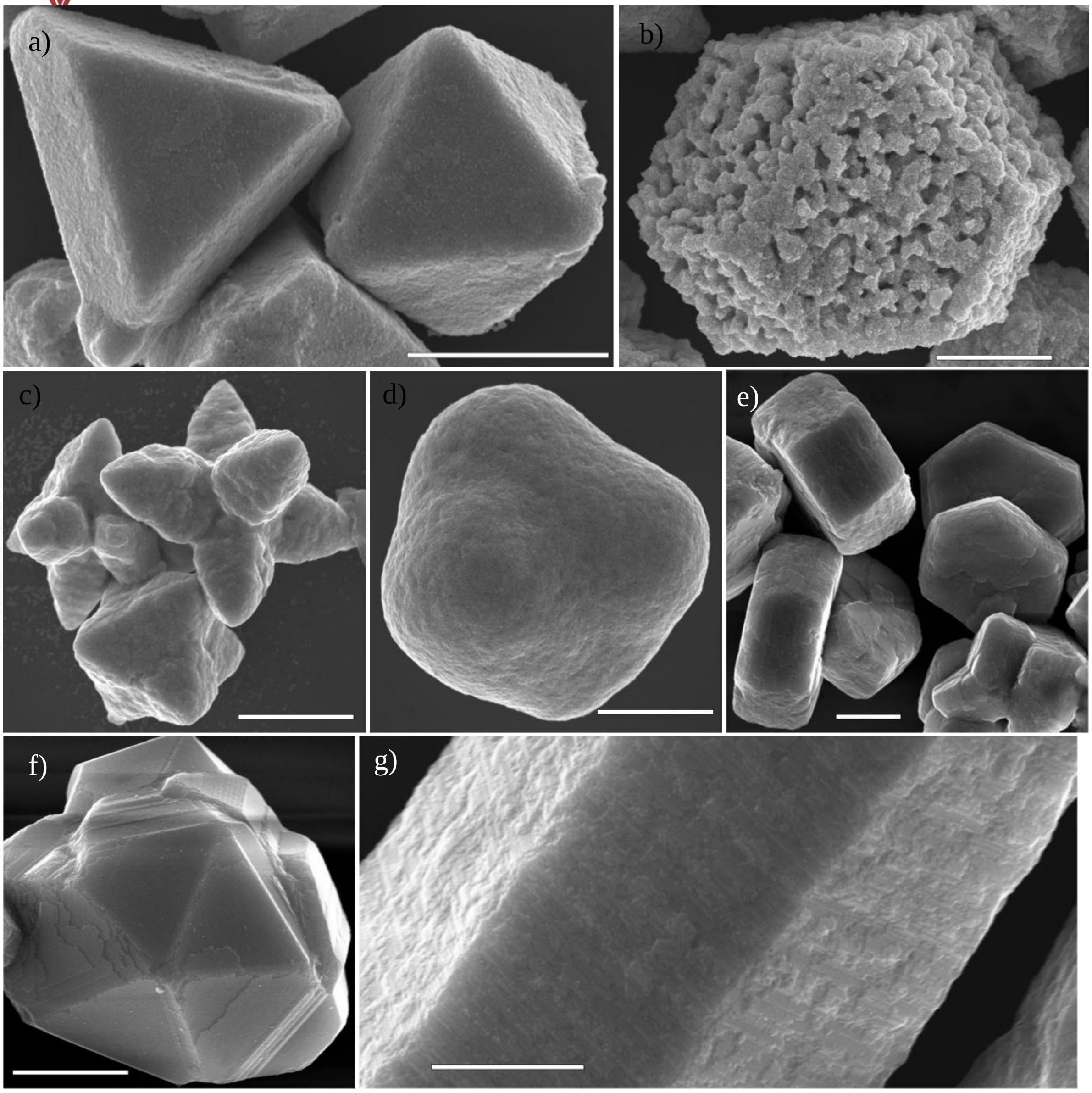

Figure 2. Some types of supracrystals obtained from gold nanoparticles: a) triangular plate (truncated tetrahedron) and octahedron; b) porous truncated octahedron; c) octahedra with (octahedral) protrusions on each vertex; d) spherically blunted octahedron. Some types of supracrystals obtained from magnetite nanoparticles: e) hexagonal plates; f) penta-twinned assembly; g) wire with hexagonal cross-section. SEM images, scale bars = 1 μm.

References:

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