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Self-Assembled 2D Protein Crystals as Templates for Ordered Metallic Nano-Arrays

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The arrangement of inorganic materials into nanoscale ordered arrays holds great promise for the production of new types of electronic, magnetic, and photonic devices. Fabricating ordered arrays on the nanoscale exceeds the limits of traditional lithographic techniques; therefore, new techniques, including those involving biomolecules such as proteins, are under investigation. We are using the heat shock protein (HSP60) from *Sulfolobus shibatae*, which self-assembles into ring structures known as chaperonins, to make ordered two-dimensional inorganic arrays. Chaperonins can be induced to form higher-order two-dimensional crystals, which can be genetically engineered into nanoscale templates that bind inorganic materials. We genetically inserted cysteine residues into the HSP60s to form two-dimensional arrays of chaperonins possessing reactive thiol groups that bind gold or platinum. Ordered arrays were created using two methods: (1) by covalent attachment of gold nanoparticles (1.4 nm Nanogold) to HSP60s prior to crystallization into arrays (Fig. 1; also see Ref. 1) and (2) by electroless deposition of $NiSO_4$ (Fig. 2) onto platinum-activated two-dimensional crystals.

Genetically engineered chaperonins containing cysteine mutations were designed, expressed, and purified as described by McMillan et. al. Two-dimensional crystals of chaperonins were made with concentrated HSP60 (1.5 mg/ml) in the presence of 4 mM ATP, 10 mM $MgCl_2$, and 0.01 % NaN_3 in 25 mM HEPES (pH 7.5) and incubated for ~ 12 hr at 4°C. Using a 1:10 dilution of the crystal suspension, the crystals were immobilized on SiO or formvar coated copper TEM grids (200 mesh). Grids were floated on the suspension for 30 s and washed in water for 30 s. The immobilized crystals on the grids were activated in 6 mM K_2PtCl_4 for 2 min followed by two 30 s washes in 25 mM NaOAc (pH 4.5). They were then metalized in a solution containing 25 mM $NiSO_4$ and 5 g/L dimethylamine borane complex (DMAB) for 30 s (Ref. 2). Reactions were immediately quenched by two 30 s water washes and the grids dried under vacuum.

Conventional TEM imaging was conducted on a LEO 912 AB at 60 kV at NASA Ames, while high resolution nanoscale imaging and characterization was conducted on a FEI Tecnai F20 operating at 200 kV at ANL. Images were recorded using STEM HAADF imaging mode, while elemental characterization of all samples was confirmed using X-ray Energy Dispersive and Electron Energy Loss Spectroscopy. Control experiments conducted without exposure to the metal salts resulted in 2D crystals without ordered metallic arrays.

We observed that the Nanogold particles covalently bound to the chaperonin template were hexagonally packed and aggregated in the cores of the chaperonins (Fig. 1). In contrast, the electroless deposition resulted in a non-uniform distribution of nickel on the chaperonin surface with regions of high density that yield the hexagonally packed array (Fig. 2).

These results demonstrate that genetically modified chaperonins can direct the formation and ordering of inorganic arrays of preformed metal particles or their precursors.

References

[1] R. A. McMillan et al., Nature Materials 1 (2002) 247.
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[3] This work was supported by the NASA Ames Center for Nanotechnology, DoE, DARPA, and by grants at ANL from DoE under contract BES-MS W-31-109-Eng-38.

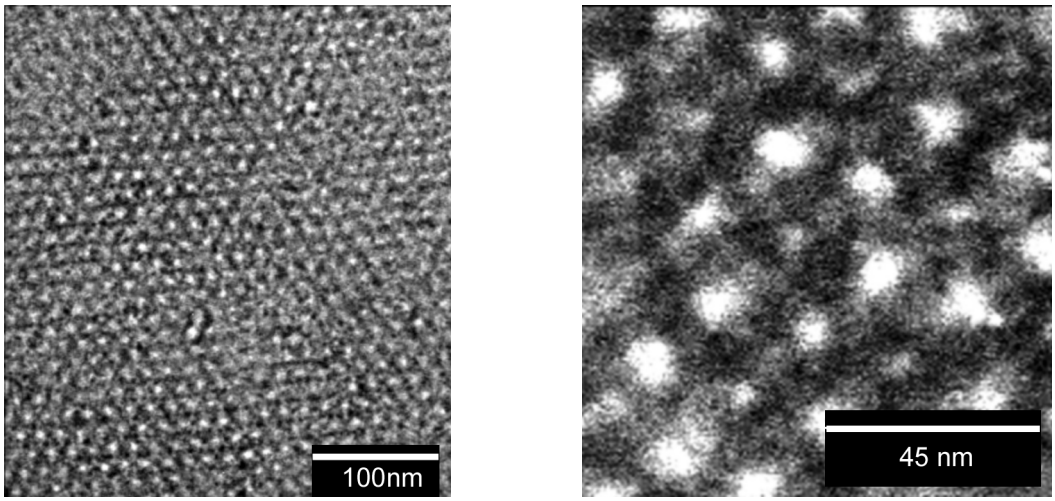

Fig. 1. Nanoscale ordered Au particles on *S. shibatae* chaperonin protein template

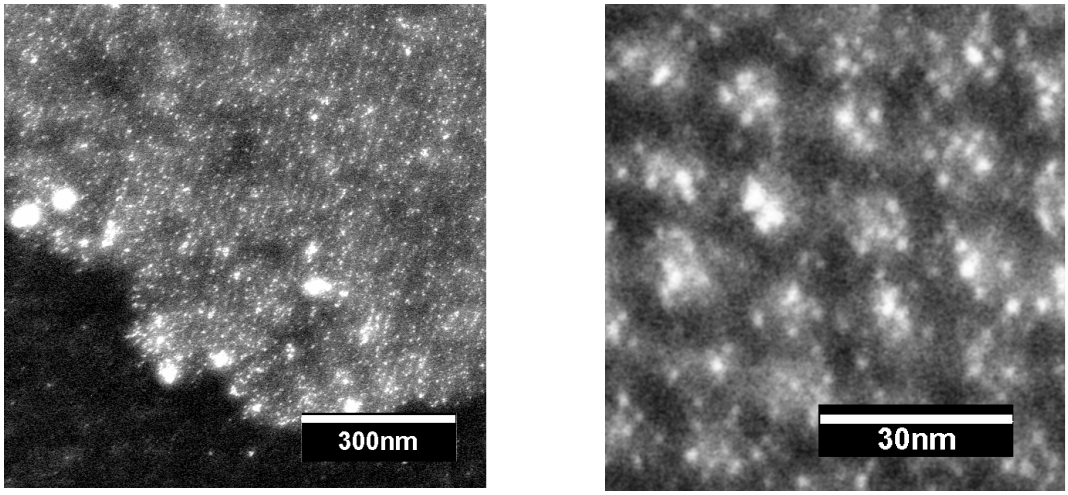

Fig. 2. Nanoscale ordered Ni particles on engineered *S. shibatae* chaperonin protein template

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