THREE-DIMENSIONAL SUPERLATTICES OF *N*-ACETYLGLUTATHIONE-PROTECTED GOLD NANOPARTICLES: EMERGENCE OF FIVEFOLD SYMMETRY

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Construction of ordered assemblies or superlattices on nanoscale dimensions is of key interest not only in electronics applications but also in fundamental nanoscience [1]. Metal nanoparticles, which can be considered as “artificial atoms”, are ideal building blocks for two- (2D) and three-dimensional (3D) superlattice structures. The organic surface protection of nanoparticles enables to control their chemical functionality and allows the collective properties of the nanoparticle superlattices to be engineered. Unlike the most successful approaches that utilize hydrophobic alkanethiols as a surface ligand [1], we have developed the syntheses of carboxylate-protected water-soluble gold nanoparticles [2]. Application of such hydrophilic nanoparticles is one of the new fields for the construction of superlattices not by weak van der Waals interaction but by strong hydrogen-bonding and/or electrostatic interactions [3]. In the present study, we report the fabrication of 3D superlattices consisting of *N*-acetylglutathione (NAG)-protected gold nanoparticles. The strategy is using hydrogen-bonding networks among the surface carboxylic acids to form nanoparticle superlattices. During the syntheses, we found that fivefold symmetric (decahedral or icosahedral) superstructures could be built from the nanoparticles.

NAG-protected gold nanoparticles self-assembled into ordered arrays or superlattices at an air/aqueous solution interface by adding a concentrated hydrochloric acid of 0.05–0.1 M [3]. Their morphology and packing structure were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) observations. The small-angle XRD profile shows several peaks (Figure 1), suggesting nanometer-scale periodicity caused by the formation of ordered arrays of NAG-protected gold nanoparticles. The constituent nanoparticles were stacked in a pattern of fcc (face-centered cubic) rather than hcp (hexagonal close-packing) with the lattice constant of 11.1 nm. The mean gold core diameter of the constituent gold nanoparticles was ~6.8 nm.

SEM observations have elucidated a variety of shapes in the 3D nanoparticle superlattices, where many of them had plate-like or complicated morphologies. In addition, some characteristic geometries of superlattices were observed; tetrahedron, decahedron, and icosahedron as shown in Figures 2a–2c, respectively. The strong emphasis is placed on the first observation of fivefold symmetry in the nanoparticle superlattices (Figures 2b and 2c). These shapes in fivefold symmetry would come from multiple twinning.

It is known that the two most typical fivefold twinning are decahedron and icosahedron. A decahedron is assembled from five tetrahedral subunits sharing an edge. An icosahedron is assembled using twenty tetrahedral subunits via sharing an apex [4]. Intrinsically, tetrahedral subunits in fcc cannot form a complete space-filling structure, so that there remains angular misfit yielding internal strain. The strain is relaxed by a reduction of surface energy up to a certain size above which transformation to single crystalline particles is expected. Hence a fivefold twined particle is commonly bounded by the lowest-energy triangular facets. In regular decahedra, they have a large surface/volume ratio, which can be lowered by truncating the edges around the common basis. One of better structures is the Marks decahedra, obtained by introducing re-entrances that separate the {100}-like facets [5a]. In Figure 2b, the observed re-entrant corners are well characterized by a typical Marks decahedron.

On the other hand, an icosahedral particle normally contains a larger strain inside due to the distortion of the intershell and intrashell distances, so that this form could be present only at small sizes in metal nanoparticles. For example, the size limit of 27.35 nm has been obtained in single icosahedral silver nanoparticles ($4–5 \times 10^5$ atoms included). Surprisingly, in Figure 2c, $1–2 \times 10^8$ nanoparticles would be included in the superlattice assuming that they are made of spheres of 7.9 nm in diameter (= center-to-center distance between adjacent nanoparticles), which correspond to 300–400 shells [5b]. This is probably due to the fact that a large relaxation of the internal strain caused by the size non-uniformity and/or surface flexibility) of the constituent nanoparticles makes the icosahedral structure much stable. The field of fivefold twinned structures is a very broad and complicated one ranging from cluster science to surface science, so that we believe that our findings will give a new development of this fascinating subject in nanoscience [6].

References:

[1] (a) Brust, M.; Kiely, C. *J. Colloids Surf. A*, **202** (2002) 175. (b) Sampaio, J. F.; Beverly, K. C.; Heath, J. R. *J. Phys. Chem. B*, **105** (2001) 8797. (c) Storhoff, J. J.; Mirkin, C. A. *Chem. Rev*., **99** (1999) 1849. (d) Burghard, M.; Philipp, G.; Roth, S.; von Klitzing, S. K.; Pugin, R.; Schmid, G. *Adv. Mater*., **10** (1998) 842.

[2] (a) Chen, S.; Kimura, K. *Langmuir*, **15** (1999) 1075. (b) Yao, H.; Momozawa, O.; Hamatani, T.; Kimura, K. *Chem. Mater*., **13** (2001) 4692.

[3] Yao, H.; Kojima, H.; Sato, S.; Kimura, K. *Langmuir*, **20** (2004) 10317.

[4] Hofmeister, H. *Fivefold Twinned Nanoparticles*; in Encyclopedia of Nanoscience and Nanotechnology, Vol. 3, ed. Nalwa, H. S.; American Scientific, Stevenson Ranch, 2004, 431.

[5] (a) Marks, L. D. *Philos. Mag. A*, **49** (1984) 81. (b) Baletto, F.; Ferrando, R. *Rev. Mod. Phys*., **77** (2005) 371.

[6] Yao, H.; Minami, T.; Hori, A.; Koma, M.; Kimura, K. *J. Phys. Chem. B*, **110** (2006) 14040.

Figures:

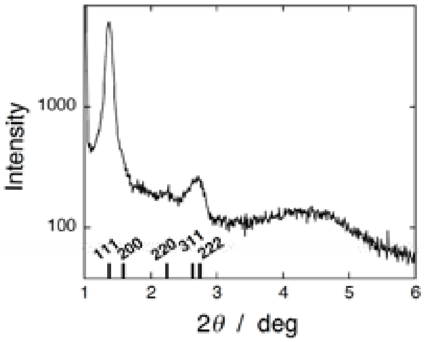

Figure 1. Small-angle XRD profile of the superlattice sample, suggesting a nanoscale periodicity caused by the formation of ordered arrays of NAG-Protected gold nanoparticles.

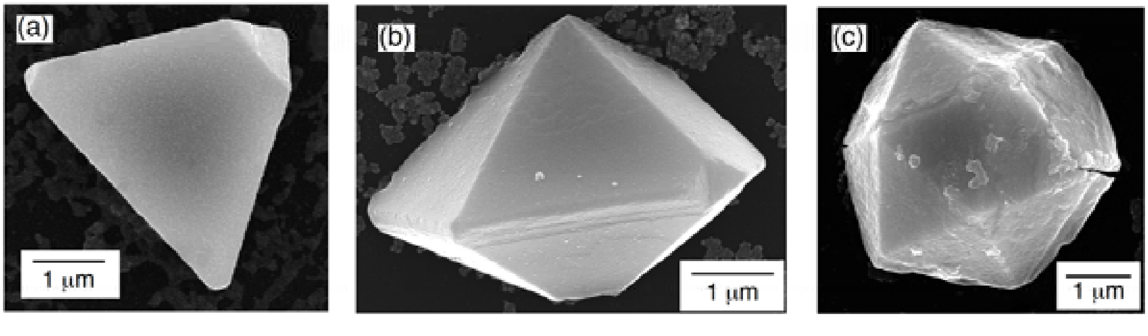

Figure 2. Nanoparticle superlattices of (a) tetrahedral, (b) decahedral, and (d) icosahedral shapes.