Disclinations in Decahedral Gold Nanoparticles: Strain Distributions by Aberration-corrected HREM

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Résumé – We will present measurements of strain distributions in Au nanoparticles determined by geometric phase analysis of spherical aberration-corrected high-resolution electron microscopy images. The results will be discussed in relation to predictions based on the elastic theory of disclinations and finite-element simulations.

1. Introduction

Recently, novel synthesis techniques have allowed precise control over the sizes and shapes of Au nanoparticles that exhibit unique optical properties [1]. We examined 5-fold-twinned decahedral (pentagonal bipyramidal) Au nanoparticles using aberration-corrected HREM, strain mapping, and electron holography. Owing to geometric constraints, these particles must be strained and/or contain defects. Several models of the strain states and expected defect structures of such decahedral particles have been proposed [2 and references therein]. We will present the first quantitative measurements of nanoscale strain distributions within these nanoparticles.

An ideal decahedral is composed of five tetrahedrons with the gold fcc structure. The tetrahedrons all share a common edge that coincides with the noncrystallographic 5-fold rotation axis parallel to [110]. Adjacent tetrahedrons are separated by twin boundaries parallel to {111} crystallographic planes. The particles have ten {111} faces. Because regular tetrahedrons, packed in this manner, are not space filling, the particles must be strained and/or contain defects.

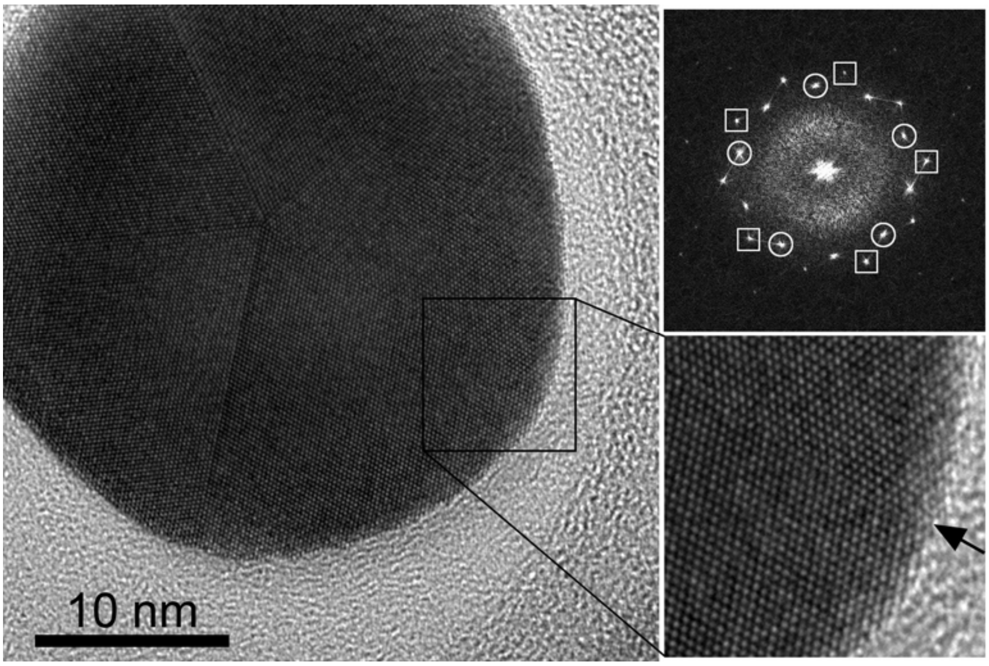

Figure 1 *– Aberration-free HREM image (a) of a 30 nm (radius) pentagonal Au nanoparticle with 5-fold twinning about the [110] axis. (b) Squares and circles in the diffractogram indicate 200 and 111 reflections, respectively, from each of the twin domains. (c) The arrow indicates the outer termination of one twin boundary from the boxed region in (a).*

2. Experimental Results

Aberration-corrected HREM imaging and electron holography were performed on the SACTEM-Toulouse, a Tecnai F20 ST (FEI) fitted with an objective-lens aberration corrector (CEOS), rotatable electron biprism (FEI), imaging filter (Gatan Tridiem), and 2k CCD camera (Gatan). Strain analyses were done using the geometric

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phase analysis (GPA) software [3]. Aberration correction provides high-contrast images necessary for precise, high-spatial-resolution strain determination. HREM images (e.g., Fig. 1) of the nanoparticles reveal that they are pentagonal in projection and composed of five domains with roughly the same size separated by twin boundaries. The interiors of the twin domains appear to be free of defects. The cores of the particles ([110] axis where the twin planes intersect) occur at their geometric center. The particles are rounded at the pentagon edges in the proximity of the twin planes. Using GPA, we mapped the strain distributions and rotations within the particles. The rotation map (Fig. 2) reveals the existence of a disclination.

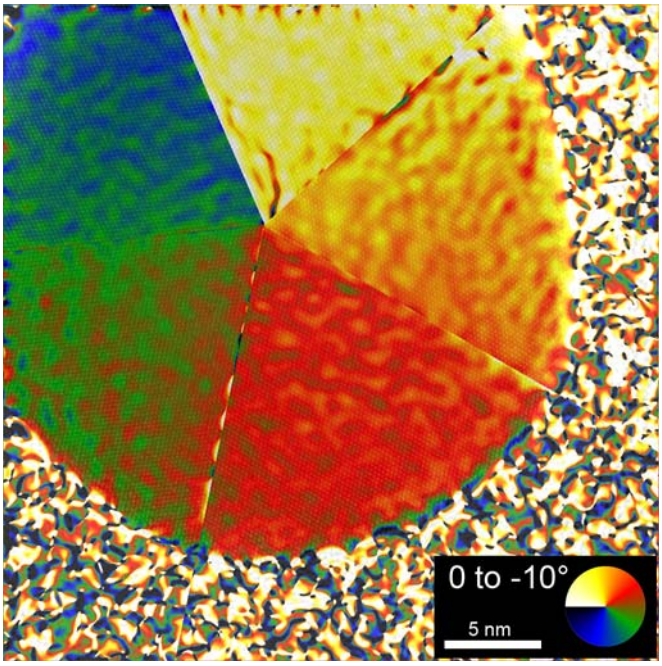

Figure 2 *– Map of the rotational distortion within the individual segments of the Au nanoparticle in Figure 1. The rotation (~1.4° for each segment) is a result of a disclination at the core of the particle.*

3. Conclusion

From dark-field TEM images, Marks [2] showed that small multiply-twinned particles like ours have inhomogenous strains. A disclination model was proposed that accounts for both the inhomogeneity and the missing wedge of material required by the particle geometry [4]. Our quantitative strain determinations reveal the actual structure of the disclinations in these particles. Furthermore, the strain maps show the degree of strain inhomogeneities present in the particles. Strain measurements will show the effects of the real shape of the nanoparticles (including rounded pentagon edges and possible re-entrant faces at the twin boundaries) on their strain state rather than the idealized strain fields predicted by the models. We will compare experimental strain distributions with those predicted by elastic theory and finite-element simulations. A complete understanding of the unique electronic, mechanical and optical properties of these nanoparticles requires detailed quantitative measurements of their strain states and atomic structure, which are accessible by aberration-corrected HREM and strain mapping [5].

4. Références

[1] A. Sanchez-Iglesias et al., *Synthesis and Optical Properties of Gold Nanodecahedra with Size Control*, Adv. Mater. **18** (2006) 2529-2534

[2] L.D. Marks, *Inhomogeneous Strains in Small Particles*, Surf. Sci. **150** (1985) 302-318

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[4] V.G. Gryaznov et al., *Pentagonal Symmetry and Disclinations in Small Particles*, Cryst. Res. Technol. **34** (1999) 1091-1119

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