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Structural Characterization of Gold Nanoparticles Using Liquid-phase 4D-STEM

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Liquid-phase transmission electron microscopy (LP-TEM) has emerged as an important tool for studying nanoscale dynamic phenomena, such as the chemical reactions and the motions of nanoparticles in liquid environment. Recent studies have monitored single particle chemical kinetics of noble metal nanoparticles using electron beam triggered oxidative etching in graphene liquid cells (GLC) [1-3]. However, particle contour tracking method via TEM images in fact only tells the projected information and would lose precise information for highly symmetric particles with allowed motions in liquid.

To address the above issue, we examine the etching process of Au nanorods. Leveraging nanorod's prolate spheroid geometry (elongated towards the major rotational axis) and its high affinity of lying flat in GLC, we were able to establish an unambiguous coordinate system defining three rotational degrees of freedom in three-dimensional (3D) space. While TEM imaging is able to completely monitor the translational motion and rotational motion perpendicular to the incident beam, it only provides a projection view for particle rotation along the short axis and is completely blind to the rotation along the long axis (major axis), shown in Figure 1(a) as angles φ and θ respectively. As a result, integrating 4D scanning transmission electron microscopy (4D-STEM), a diffraction method capable of reconstructing real-space images, with LP-TEM enables systematically nanoparticle orientation mapping in reciprocal space and nanoparticle contour reconstruction in real-space. In order to determine the particles' orientations and to construct their rotation trajectories, we utilized automated diffraction pattern recognition and indexing to efficiently process large 4D-STEM datasets [4]. Similar studies were also conducted for five-fold twinned (decahedron) nanoparticles, regarding how the internal strain induced by the particle geometry ties to their thermodynamic stability and catalytic activity. Our preliminary results of Au decahedron particles in dry state indicate simultaneous lattice rotation and strain distributed non-uniformly across five tetrahedron motifs, showing agreeing details with the literature yet with underlying complexity and heterogeneity that previous studies have not had access to [5, 6]. By using liquid-phase 4D-STEM, we aim to resolve strain atomic dynamics via layer-by layer fashion in etching solution to further exploit the potential of this unique combination of techniques [7].

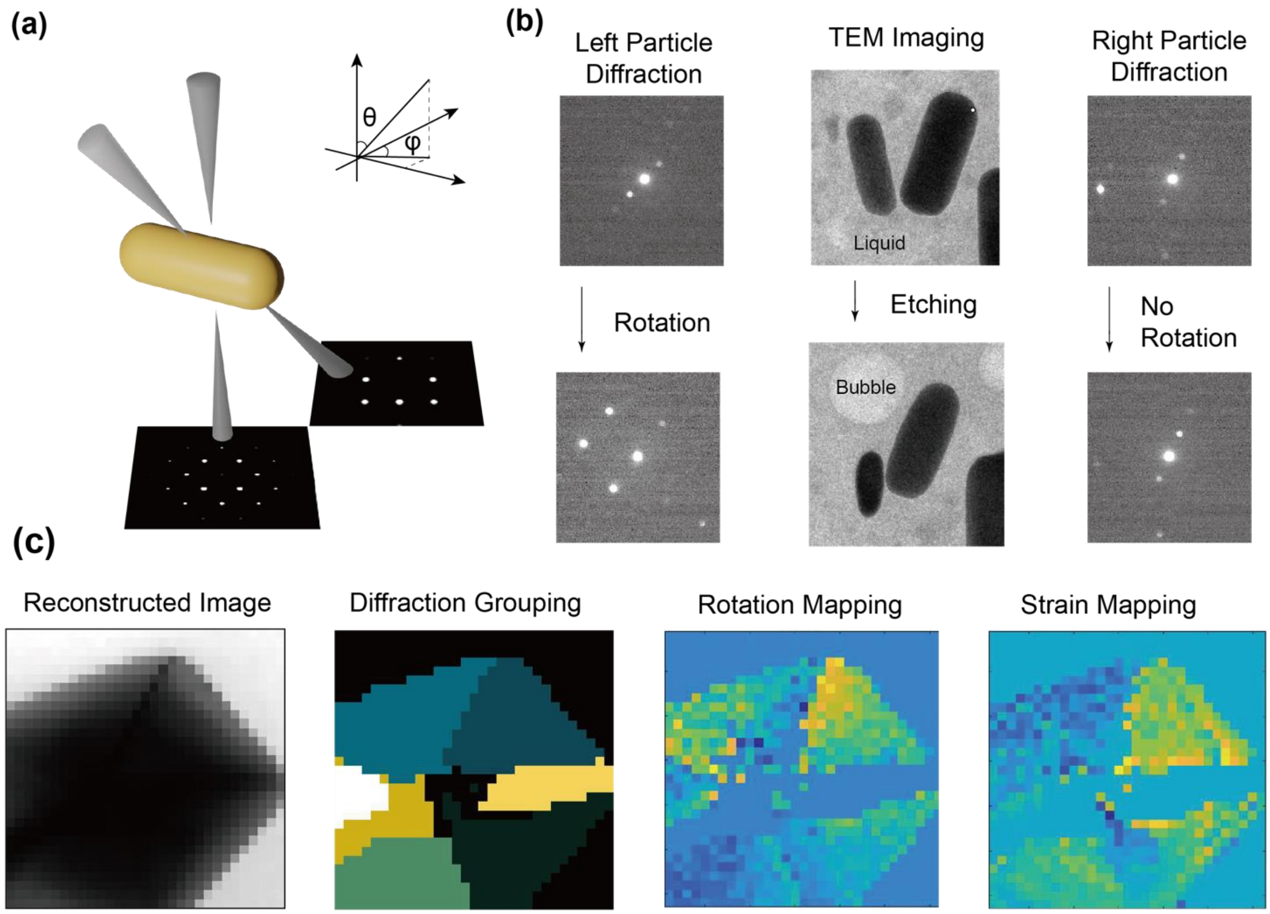

Figure 1. Schematics of structrual characterization of Au nanoparticles: (a) particle orientation tracking via diffraction from different angle with respect to incident beam, (b) particle rotations observed in GLC and their corresponding diffraction patterns, and (c) reconstructed bright-field image and mappings of nanoparticle lattice rotation and strain using 4D-STEM.

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