ATOMIC ALIGNMENT OVER SUPERLATTICES OF WATER SOLUBLE AU NANOPARTICLES

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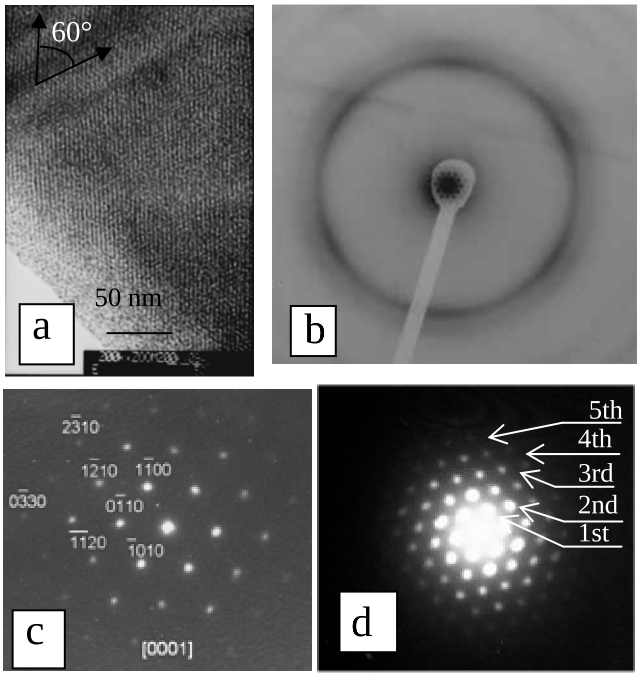
A quality superlattice made of hydrophilic Au nanoparticles was grown at an air/water interface within several days or a week. A self-correcting process took place during this period. The superlattice revealed both narrow angle and wide angle electron diffraction, indicating that there were both translational and orientational ordering in a superlattice. A model structure of this superlattice was constructed based on a truncated octahedral shape at an atomic level. The ordering misfit angle was derived from the analysis of the crescent pattern in a wide-angle diffraction region.

Mercapto-succinic acid-coated gold nanoparticles in the average size of 3.7 nm was prepared by a procedure basically similar to that described in the former work. A superlattice formation was also followed by the published method. After 3-5 days under room temperature, the crystallization took place in a range of HCl concentration (0.3±0.2M) giving numerous faceted crystals with micrometer sizes. These gold nanoparticle crystals were transferred to silicon(XRD), glass(optical), amorphous carbon(TEM, SAED) and NaCl(FTIR) substrates for analysis.

Several morphologies are noticeable such as pyramidal, triangle and hexagonal plate in an optical micrograph of the Au quality superlattice of 10 μm in size. Figure 1a is the magnified TEM image of one thin plate, in which six fold symmetry is obvious as indicated by 60-degree arrows. Figure 1b is WAED from the sample of Figure 1a. There are central spots in NAED(c and d) as well as the six-fold crescent in WAED region, which is successfully indexed as fcc metallic gold. A magnified image (d) shows even 5-th Bragg diffraction spots. It should be noted that the diffraction spot in WAED region is not a point nor arc in Fig.1b but crescent shape and that both WAED and NAED have exact six fold symmetry. We should also note that the relative orientation direction of WAED to NAED spot. Figure 2 illustrates how atomic lattice alignment in a superlattice reflects to ED. Case a stands for the situation of both translational and orientational orderliness, spots in NAED are arising from translational alignment of particles, which are surrounded by peripheral spots from atomic scale regularity. Case b is the translational ordering with no atomic orientational alignment, which comprises peripheral rings from random orientation of atoms. Note that rings or spots in WAED region can classify these two cases. Thus based on the ED patterns, we constructed a structural model of Au nanoparticle superlattice. If we accept the truncated octahedron (TO) morphology as the shape of the Au cores, the component Au nanocrystals of average core diameter 3.65 nm consist of 1709 atoms, which are close to the observed size, 3.7nm. That is, there is a magic number even for a large size particle comprised of thousand of atoms.

The resultant three-dimensional structure is shown in Figure 3a. Inverse space projection of each atom is presented in Fig.3b, in which we notice a lack of six-fold symmetry. The two-dimensional projection of this model shows that the core dimension is 3.26 and 3.30 nm for different direction suggesting that it is possible to rotate 60 degree for randomly selected particles. After allowing this rotation, the estimated ED becomes hexagonal symmetry as shown in Fig.3c. We further analyzed the structure of crescent diffraction spot and found that there is 0.5 degree misfit among neighboring particles. Detailed analysis will be presented on the session.

References:
[1]Seiichi Sato, Suhua Wang, Keisaku Kimura, J.Phys.Chem.C(2007) in press.



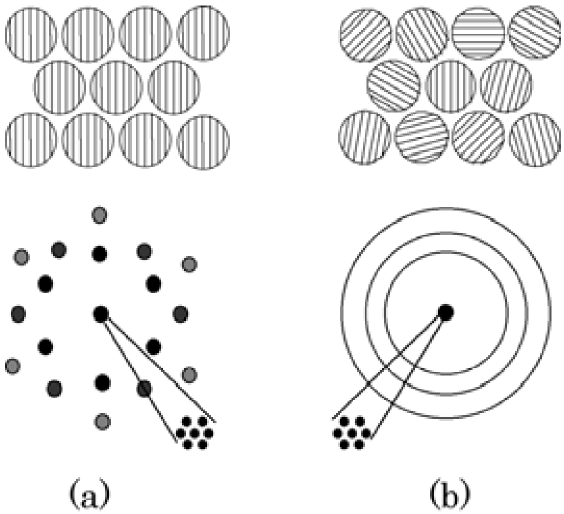


Figure 2 Model of perfect superlattice (a) and orientation randomized crystal (b). Above; real space image and below; inverse space image.

Figure 1 HRTEM(a), TED(b), NAED(c, d) of superlattice of MSA-Au.

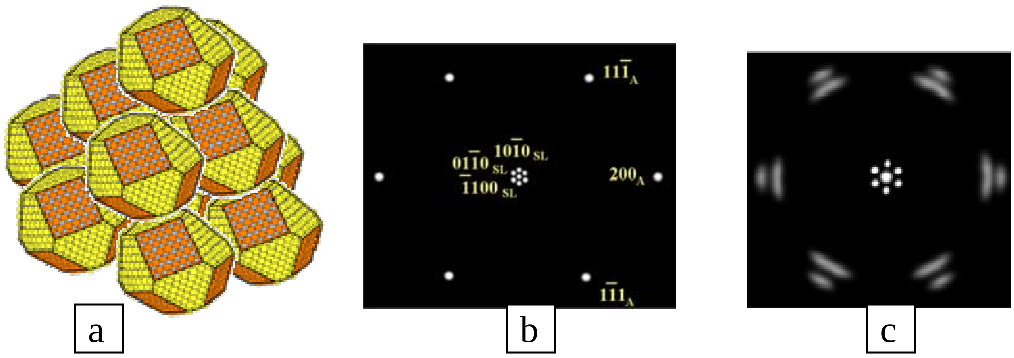


Figure 3 A model structure of MSA-Au superlattice (a), and it's TED(b). In order to fit the observed WAED(Fig.1b), the orientation of arbitrarily selected particle in a superlattice must rotate just 60 degree giving Fig.3c model ED.