Due to the low flux available on neutron sources, huge crystals (volume > 1mm³) were usually required for neutron diffraction data collection. Within our collaboration with the Institut Laue Langevin (ILL) in Grenoble-France, this stringent bottleneck can now be overcome successfully by an ab-initio perdeuteration followed by crystallization in D2O and by mounting the resulting crystals in quartz capillaries tightly closed. The perdeuterated crystals have to be sheltered always from wet air moisture. A perdeuterated human-Aldose Reductase -NADP+-inhibitor IDD594 complex [h-AR(D)-36kDa] tiny crystal with a volume of 0.15mm³ was measured on the LAue Diffractometer LADI-I (external imaging-plate reading) at a useful resolution of 1.85Å. Both data collection parameters are given together with the resulting statistics. For X+N refinements purposes on [AFP(D)], results are reported for an X-ray data collection done also at 293K (resolution 1.05Å) on beamline ID29 at the Synchrotron ESRF within the Partnership of Structural Biology (PSB) in Grenoble-France. The ability of neutron diffraction data collection at room temperature from tiny crystals opens the way to study a larger number of biologically important proteins.

Keywords: neutron protein crystallography; aldo-keto reductases; antifreeze proteins

An in-situ study of the silver nanoparticle self-assembly at the air/water interface was performed in a fast tracking mode. The spherical nanoparticles were prepared by inverse micelle technique in the form of a colloidal solution that was applied on the water surface. The nanoparticles composed of a metallic core of the 7±0.7 nm diameter and a surfactant shell (oleic acid and oleylamine) to prevent agglomeration exhibit plasmon resonance close to 500 nm. The grazing-incidence small-angle X-ray scattering (GISAXS) was applied to identify principal stages of the nanoparticle monolayer formation during compression of the nanoparticles in the Langmuir-Blodgett trough at a constant barrier speed of 26 cm/min. The GISAXS measurements were performed at ID10B beamline at ESRF, Grenoble. The X-ray beam of the size 300x100 mm² and the energy 8 keV hit the air/water interface at 0.35º grazing angle of incidence. A fast 2D X-ray detector PILATUS 300K provided a series of GISAXS frames to track immediate response to compression of the nanoparticle Langmuir film. Hence, all relevant intermediate phases including those far from the equilibrium could be identified and related to the surface pressure - area isotherm. The formation of nanoparticle monolayer starts with coalescence of free self-assembled nanoparticle islands with the 2D hexagonal close-packed order inside as documented by Bragg rods in the GISAXS pattern (stage I). In stage II, the surface pressure starts to grow as the proceeding island coalescence forces the larger assemblies to get into contact. The stress accumulated at the assembly boundaries is partly relieved by the nanoparticle re-arrangements to form a continuous close-packed monolayer with local hexagonal order preserved from the original islands. The end of stage II is suitable for the transfer onto a solid substrate to deposit a high-quality nanoparticle monolayer over large area. In stage III, the accumulated stress accelerates the surface pressure growth and the elastic modulus goes to a maximum while the nanoparticle lattice gets temporarily squeezed by approximately 0.1 nm and the lattice disorder increases as documented by the Bragg rod maximum position and width evolution. This highly non-equilibrium phase preceding the monolayer collapse has never been observed before. The collapse (stage IV) takes place by flipping up the nanoparticles and the second layer formation. New modulations appearing along the Bragg rods suggest the AB-like crystallographic stacking and enhanced paracrystalline-like disorder. The Langmuir film expansion runs irreversibly by decomposition into bilayer islands without observable changes in the nanoparticle order inside. The results obtained have direct implications for preparation of plasmonic nanoparticle templates. This work was done during implementation of the project Research and Development Centre for Advanced X-ray Technologies, ITMS code 2622020170, supported by the Research and Development Operational Programme funded by the ERDF.

Keywords: GISAXS; Langmuir monolayers; nanoparticles