Scattering studies of nanoparticles and their assemblies: Size-selective cluster and DNA-programmed nanoparticle cluster

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Abstract

Small-angle x-ray scattering (SAXS), which has been popular for studying various nanostructures of polymers and biomolecules, is now gaining new attention from many other fields dealing with nano-catalysts and self-assemblies of organic or inorganic particles due to its improved capability with a synchrotron x-ray source. Grazing incidence small-angle x-ray scattering (GISAXS)[1,2] is a thin film or surface version of SAXS and is used to determine the shapes, sizes and spatial correlation of nanoparticles on the substrate, as well as in the substrate.

In this presentation, two on-going research projects utilizing SAXS and GISAXS are introduced. The first example is the size-selective clusters investigated using GISAXS. It is known that the catalytic activity and selectivity of the nanoparticles strongly depend on particle size, composition, and shape, as well as the substrate material. Their catalytic properties can be strongly altered, and the catalytic activity can be lost due to the sintering process taking place at elevated temperatures or upon exposure to mixtures of reactive gases. In order to correlate the catalytic activity with the structure of nano-clusters, in situ simultaneous GISAXS and mass spectrometry equipped with gas-flow control have been proposed and designed. We found that sintering behaviors of size-selective metallic nanoparticles such as Pt and Au under a reactive gas environment are quite different from those under vacuum. Especially, Ag particles on a substrate significantly change their orientation at RT only with the introduction of reactant gases.

Secondly, DNA programmable crystallization of Au nanoparticles are also of interest.[3] While it was shown more than a decade ago that DNA oligonucleotides can be attached rationally to Au nanoparticles to direct the formation of larger assemblies, the conceptually simple yet powerful idea that functionalized nanoparticles might serve as basic building blocks that can be rationally assembled through programmable base-pairing interactions into highly ordered macroscopic materials remains poorly developed. So far, the approach has mainly resulted in polymerization, with modest control over the placement of, the periodicity in, and the distance between particles within the assembled material. Recently, we demonstrated that DNA can be used to control the crystallization of nanoparticle–oligonucleotide conjugates to the extent that different DNA sequences guide the assembly of the same type of inorganic nanoparticle into different crystalline states. In this presentation, several factors that we found critical to govern the process are discussed as well as the contribution of synchrotron SAXS.

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