Self-assembly of gold nanorods in ordered spherical supraparticles

J.E.S. van der Hoeven1,2, Y. Liu1, M. Bransen1, D.A.M. de Winter1, M.A. van Huis1, P.E. de Jongh2, A. van Blaaderen1

(1) Soft Condensed Matter, Utrecht University, Utrecht, Netherlands
(2) Inorganic Chemistry and Catalysis, Utrecht University, Utrecht, Netherlands

Gold nanoparticles exhibit interesting optical properties which arise from their localized surface plasmon resonance. In particular anisotropic Au nanoparticles, such as Au nanorods (NRs), have enhanced and highly tunable plasmonic properties due to their longitudinal surface plasmon resonance in the visible and near-infrared range of the spectrum. This makes Au nanorods suitable materials for numerous optical applications such as surface-enhanced Raman spectroscopy (SERS) [1], data storage [2], photo catalysis and medical photo thermal applications. Recently, it has been shown that performance of AuNRs in Raman spectroscopy can significantly be enhanced when placing the NRs in close proximity in large colloidal crystals, whereby plasmonic hotspots of the individual NRs overlap and strongly enhanced plasmonic hotspots are created [3].

Here, we present the synthesis of spherical colloidal crystals, so-called supraparticles, of variable size consisting of silica coated AuNRs (Figure 1). The aim of the study is to compare supraparticles with and without overlapping plasmonic hotspots between the AuNRs in their performance in Raman spectroscopy. To this end, silica coated AuNRs with either a 15-20 nm thick mesoporous silica shell or a 3-4 nm thin silica shell were assembled in supraparticles. The self-assembly was done by using a solvent evaporation method [4], whereby a polar dispersion of rods was emulsified in a larger apolar phase. By slowly evaporating the polar phase, the AuNRs in the shrinking droplets assembled into spherical supraparticles. The 3D-structure of these assemblies was studied in detail with advanced electron microscopy techniques such as HAADF-STEM tomography and FIB-SEM slice and view, allowing us to track the position and orientation of the NRs [5]. First, we show the aspect ratio of the rods strongly influences the degree of order in the orientation of the rods, where the orientation of the rods changes from random- to smectic order when increasing the aspect ratio of the rods. Second, we compared the enhancement of crystal violet in Raman spectroscopy in the presence of supraparticles with and without overlapping hotspots and detect much higher Raman signals in the structures composed of thin silica coated AuNRs compared to the supraparticles of thick silica coated AuNRs.

Figure 1. Electron microscopy images of ordered spherical supraparticles synthesized via the self-assembly of 3-4 nm thin silica coated Au nanorods

References
1- M.N. Sanz-Ortiz, ACS Nano, 9 (2015), 10489–10497
2- P. Zijlstra et al., Nature, 459, (2009), 410–413
3- C. Hamon et al., Nanoscale, 8, 2016, 7914

Corresponding author email: j.e.s.vanderhoeven@uu.nl