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Structure and dynamics of poly ethylene glycol coated Au nanoparticles

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Polymer-capped gold nanoparticles (AuNP) have many peculiar aspects like quantum size effects and single electron transitions. Their properties are highly dependent on their size and shape and upon spatial relationship of one particle to another. Coating nanoparticles with polymers tethered to their surface by means of specific ligands stabilizes them, and allows functionalization for specific applications in nanotechnologies, biology and biomedical studies[1], and can promote the bottom-up approach to the fabrication of nanostructures.

We studied the structure and the dynamics of a key class of polymer-capped AuNP, those coated with poly ethyleneglycol (PEG AuNP). A novel synthesis was developed by ligand exchange procedure, which ensure the production of NP with little excess of (expensive) functionalizing ligand and high stability[2]. When dissolved in water, PEG AuNP are typical example of mesoscopis solute in microscopic solvent and the thermodynamic conditions of the solution depend on the extension and local properties of the solute-solvent interfaces, like biological molecules (e.g. proteins, ribosomes). However, understanding the relation between the structure, the dynamics and the function of biological molecules is, to say the least, not straightforward, since they are composed by a combination of functional groups, with different affinity and interacting differently with water, thus influencing the properties of the solvent molecules in a way that is difficult to rationalize. On the other hands, polymer coated NP have more homogeneous interfacial properties that can be modulated precisely by varying the type, the length, and the areal density of the grafted polymers, or characteristics like temperature, salts content of the solution, and can serve as simpler model systems to draw a structure-dynamics relationship map on the mesoscopic scale, that can be then possibly applied to more complex biological systems.

The structure PEG AuNP were studied by combining transmission electron microscopy (TEM), mass density, termogravimetric analysis (TGA) and small angle neutron scattering (SANS) as a function of temperature, and of the length of the interfacial polymer chains. PEG Au NP functionalized with short (PEG400) and long (PEG2000) polymer reflected substantial differences in the structure of the polymer at the interface. The Au NP functionalizes with the longer PEG showed a considerable gradient in the density of the polymers in the corona and in their hydration. A significant effect due to the solvent isotopic substitution was also envisaged. The dynamics of PEG AuNP in the nanosecond timescale was also studied by neutron spin echo (NSE) spectroscopy. NSE experiments gave evidence of two dynamical processes, one related to the translational diffusion of the nanoparticles (which agrees with the one evaluated by Stokes-Einstein equation), and a faster due to internal motion of the polymer chains, whose characterization is in progress.

References

1. M-C. Daniel, D. Astruc, Chem. Rev. 104, 293-346 (2004)
2. S.Rucareanu, M. Maccarini, J. L. Shepherd, and R. B Lennox J. Mater. Chem 18,5830 (2008)

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