New strategies of colloidal stabilization of nanoparticles for applications in aqueous media

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Since it was discovered that metallic and semi-conducting nanoparticles have unique optical properties, many biomedical applications have been proposed for these nanomaterials in the fields of imaging, sensing, and therapy. All these biomedical applications require water dispersability and long term stability of the nanoparticles at high ionic strength. In addition, the need to develop "green" catalytic processes also demands new water dispersable nanoparticles. The synthesis of well-defined metallic and semi-conducting nanoparticles are usually achieved in organic solvent, producing particles with a hydrophobic surface. Thus, the obtention of water-dispersible nanoparticles by direct synthesis or transfer is still a challenging task.

Our group develops new strategies to produce various water dispersible metal or semi-conducting nanoparticles (Au; Pt; Ag, ZnO). The nanoparticles can be synthesized *in-situ*, transferred from organic solvent or synthesized in water and stabilized *a posteriori*. We focus on the design of stabilizers. The properties (catalysis, toxicology...) of the so-formed water-dispersable nanoparticles are investigated (Figure 1).

We will particularly describe the use of amphiphilic stabilizers. Indeed, the self-assembling properties of amphiphilic compounds provide (i) enhanced adsorption at the surface of the particles; (ii) stabilization through non-covalent interactions with the surface, that avoids modification of the nanoparticles properties and allows direct generalization to particles made of various materials. We have investigated the stabilizing efficiency of various amphiphilic compounds with a diblock A-B structure (A= hydrophilic, B= hydrophobic), such as surfactants and diblock copolymers, or with a triblock A-B-A structure: bola-amphiphile surfactants, triblock copolymers[3], core-multishell hyperbranched polymers.

Triblock amphiphilic structures act as efficient stabilizers even in conditions where the formation of self-assembled objects (micelles, vesicles...) does not occur in solution (for instance at concentrations lower than the critical agregation concentration). The predominent role of the length of the hydrophobic B segment, for the colloidal stability is clearly evidenced. In addition, the use of bolaamphiphile surfactants (notedwith charged polar head and long alkyl chains (n>12) allows one to precipitate and redisperse the nanoparticles at will[4]. Long term stability in condition of high ionic strength can be achieved by an appropriate choice of non ionic A-B or A-B-A copolymers, for instance made of hydrophilic oxyethylene and hydrophobic oxypropylene segments.

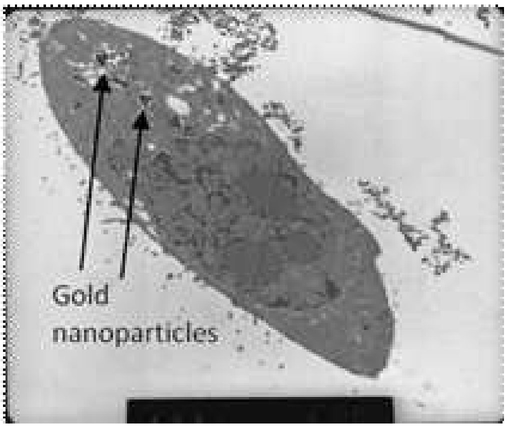
Finally, core-multishell polymeric structures designed with a careful choice of their external groups exhibited a remarkable behaviour, combining extremely long term stability with dispersability of hydrophobic and hydrophilic nanoparticles in a wide range of solvents (from water to chloroform, see Figure 2).

In all cases, water-dispersability and stability are investigated in relation with the chemical structure of the stabilizers in order to optimize the design of efficient stabilizers.

References:

Figures:

Figure 1: Cellular uptake of gold nanoparticles coated by triblock copolymers (PEO-PPO-PEO)



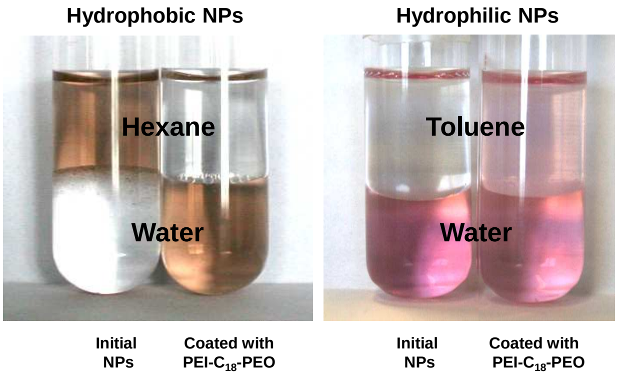


Figure 2: Left: phase transfer of hydrophobic AuNPs from hexane to water before and after capping with a core-multishell polymeric structures (PEI-C_{18}-PEO). Right: partial phase transfer of hydrophilic AuNPs from water to toluene before and after capping with PEI-C_{18}-PEO.