

Synthesis of thiol-functionalized polymers and grafting to silver and gold nanoparticles.

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The preparation of novel functionalized polymers and its combination with metal nanoparticles to produce hybrid materials is a research area of great interest for nanotechnological applications. The fact that polymers and block copolymers could be used as capping agents, reducing agents [1] and templates [2], to name just a few, for the synthesis of metal nanoparticles make them an invaluable tool for the development of new materials.

Synthesis of polymers and copolymers with well defined composition and functionalities may be performed with controlled living radical polymerization method. Because of the properties of sulfur containing functional groups, organic molecules with such groups have attracted significant attention especially for the chemical interactions with some metal nanomaterials. As a matter of fact ligand functional polymers may be used for the dispersion of metal nanoparticles passivated by thiolate ligands.

Different strategies may be used for the preparation of such metal-polymer hybrids which can be grouped into two main classes:

- a) In situ synthesis of metal nanoparticles with the functionalized polymer.
- b) Preparation of metal nanoparticles by a convenient route and then assembly with the polymers.

A series of homopolymers and styrene-containing block copolymers were prepared by atom transfer radical polymerization (ATRP). In a second step, the polymers were functionalized by reaction with sulfur containing nucleophilic precursor of the thiol to form thiol end-functionalized polymers.

In the first approach the metal nanoparticles were synthesized in the presence of the functionalized polymers. This procedure has produced metal nanoparticles with the drawback of a high polydispersity in the mean size. The well-known complementary functionality between the thiol groups of the polymer and the metal surface of the metal species allows the stabilization of nanoparticles and avoid aggregation phenomena.

Following the second approach, gold and silver nanoparticles were prepared by different methods and then the protecting agents replaced by the functional polymers.

FTIR and UV-Vis Spectroscopy were used to follow the ligand exchange process, whereas TEM enable us to study the spatial distribution and assembly of the metal nanoparticles. Depending on the length of the polymers a control of the arrangement and ordering of nanoparticles could be achieved.

References:

- [1] C.E. Hoppe, M. Lazzari, I. Pardiñas-Blanco, M.A. López-Quintela, *Langmuir*, **22** (2006) 7027.
- [2] M. Lazzari, M.A. López-Quintela, *Adv. Mater.*, **15** (2003) 1583.