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NOVEL CHEMISTRY FOR THE SYNTHESIS OF ORGANIC-INORGANIC HYBRID NANOPARTICLES MEDIATED BY SUPERCRITICAL CO_2.

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Abstract

Inorganic nanoparticles with an organic functional shell have attracted much interest due to their application as catalytic or biological materials. Beyond providing solubility and preventing aggregation, the organic shell can also induce selectivity in catalytic reactions[1] and compatibility in physiological systems as well.[2]
Most often, inorganic nanoparticles are prepared by solution chemistry from soluble metal precursors.[3] The organic solvents used in the synthesis of lipophilic-functionalized nanoparticles are chosen to suit the synthesis process, that is solubilize metal precursors, reducing agents and stabilizers, and to prevent aggregation as well.

Supercritical CO_2 ($scCO_2$) offers regularly an alternative medium in replacing organic solvents in many fields. Nevertheless $scCO_2$ has been used for the synthesis of functionalized hybrid organic - inorganic nanoparticles occasionally only, due to the low solubility of many organic stabilizers in $scCO_2$.[4] Indeed, only specific organic compounds are entirely or partially soluble in this medium, mainly fluorous- and siloxane-based molecules. Presently, approaches used to form stabilized nanoparticles in $scCO_2$ depend on the solubility of reactants in the medium as methods developed for chemistry in liquids.

We propose to discuss the synthesis of organic-inorganic hybrid nanoparticles in $scCO_2$, in which reactants need not to be soluble.[5] The decisive factor for the selection of metal precursors and functionalizing agents was not their solubility, as in most of previous studies, but the desired properties of the polymer - nanoparticle hybrid.

This approach will be illustrated by the synthesis of palladium and silver nanoparticles stabilized with dendritic polymers, synthetically well accessible with a broad range of functionalities (perfluoroalkyl, perfluorooligoether, polysiloxane, non-fluorinated alkyl and oligoethylene glycol moieties).[6] The synthesis and solubility in $scCO_2$ of these polymers has been reported previously.[7] The nanoparticle synthesis is based on the reduction of palladium acetylacetonate ($Pd(acac)_2$) and silver acetylacetonate (Ag(acac)) with H_2 in $scCO_2$ in the presence of the dendritic polymer.

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