Preparation of functional hybrid palladium nanoparticles using supercritical fluids: a novel approach to detach the growth and functionalization steps†

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We report a novel and versatile approach to control separately the growth and functionalization steps in preparing functional nanomaterials. The applicability of this method was demonstrated with the preparation of palladium nanoparticles capped with thiol or stabilized with ionic liquid.

Potential applications of inorganic nanoparticles (NPs) with a functional organic shell have induced tremendous amount of studies, either to control size and shape of the NP core and/or to choose the chemical structure of the stabilizing ligand shell.[1] This allows us to tailor the NPs specific properties towards the many foreseen applications such as electron transfer applications (electronics, catalysis, electrochemistry, photochemistry) or lock–key interaction applications (recognition, gene delivery, sensoric operation). Nevertheless, methods generally used present a lack of flexibility and two main drawbacks are generally found: (i) the control on one NP parameter like core size is often obtained through limitative growth conditions that necessitates the use of specific solvent, reducing and functionalizing agent; (ii) the surface modification of the shell (by exchange or chemical reaction) was restricted to a limited number of cases.[2] Today there is a great challenge to develop alternative methods that provide convenient access to ligand-functionalized NPs for which the choice of the characteristics of the hybrid NPs is targeted by the specific property to be achieved.

We now report on a versatile synthetic method capable of producing a wide variety of NPs possessing tunable peripheral chemical functionalities by separating the growth and the functionalization steps. The principle of this new approach is illustrated in Fig. 1.

The control of inorganic core characteristics is insured by using supercritical fluids (SCF) as a reaction media without using a stabilizing agent (Fig. 1, (1)). Few recent review papers highlight the potentiality of this method to produce in a controlled fashion dry NPs without the use of surfactants.[3] These NPs have generally (i) a narrow size distribution adjustable between 1 and 100 nm, (ii) a composition among the metals, semi-conductors, oxides and to some extend nitrides, (iii) a controlled shape (0D or 1D[4] nanomaterials) and (iv) a crystallinity rate from an amorphous phase to a specific crystalline structure. This control is obtained in playing with the main operating parameters of this method (pressure, temperature, nature of solvent(s) and reagent(s), concentration of reagents and residence time) to master the reaction kinetics and the thermodynamical properties of the reaction media. The use of SCF as reaction media for the growth of NPs allows us to obtain naked NPs with the control of the size, shape, crystallinity and composition (Fig. 1, (1)). However dried NPs are obtained in most cases agglomerated[5] and SCF based methods has been used for the synthesis of functionalized hybrid organic/inorganic nanoparticles only occasionally.[6] Resuspension of NPs in solution as individual NPs is also difficult. Here, in order to prevent agglomeration, we spray the NPs into a glass vessel containing a functionalizing agent in solution at the normal conditions of pressure and temperature. This step is the second part of our synthesis process to functionalize NPs with a wide range of ligand selection (Fig. 1, (2)). The aforementioned possibilities for synthesizing inorganic NPs using supercritical fluids added to the chemistry that can be carried out in the functionalization vessel give to this ''Nanofunct'' approach a huge versatility.

The synthesis of palladium NPs functionalized with a thiol ligand was chosen as a model system. Indeed, the work of Brust and Schriffin in their toluene phase separation of alkanethiolate-monolayer-coated gold NPs of 1–3 nm, has opened up a whole new field in materials science.[7] Due to

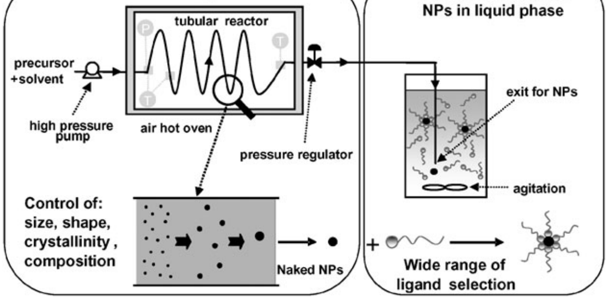

Fig. 1 Illustration of the synthesis method of functional nanoparticles (NPs) based on the separation of growth and functionalization steps (see ESI†).

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the variety of hydrophobic ligand shells accessible and their extraordinary stability, these alkanethiolate-monolayer protected nanoclusters provide versatile precursors for the fabrication of nanoscale systems.[8]

In a typical experiment, the thermal decomposition reaction of palladium trifluoroacetate was carried out in a continuous plug–flow reactor at constant pressure (20 MPa) and temperature (250 °C) with a residence time of 10 s. Supercritical acetone was chosen as the best media to transport the NP palladium precursor; the concentration of palladium was 6×10^{-3} g $g_{acetone}{}^{-1}$. The obtained NPs were sprayed into the glass vessel filled with a solution of heptadecafluoro-1-decanethiol as the functionalizing agent. Yet, to demonstrate the key role of thiol during the functionalization step, the same experiment was performed in spraying NPs in a vessel containing only acetone without stabilizing agent.

In both cases, a black powder could be isolated by simple evaporation of the solvent used in the functionalization vessel and was easily redispersed. X-Ray Diffraction (XRD) pattern and X-ray photoelectron spectroscopy measurements were performed; these results confirmed the cubic face centered structure of metallic palladium NPs (see ESI†). Palladium NPs were characterized by Transmission Electron Microscopy (TEM). The TEM micrograph shows well dispersed NPs collected in presence of heptadecafluoro-1-decanethiol with a fairly narrow size distribution of 2.1 ± 0.4 nm (Fig. 2a). For the non-functionalized NPs, the TEM grid was covered by spherical aggregates with a wide size distribution of 98 ± 41 nm (Fig. 2b). These aggregates are composed of self-assembled NPs with a mean size of 3.2 ± 0.7 nm (TEM micrograph of 1 aggregate as inset in Fig. 2b, see ESI† for size distribution).

Furthermore, concerning the functionalization step, TEM observations (Fig. 2) suggested that the use of the thiol-based stabilizer prevents further growth and aggregation of the NPs in the functionalization vessel. This was confirmed by Dynamic Light Scattering (DLS) measurements on these colloidal solutions. Hydrodynamic diameters were, respectively found to be 8 ± 3 nm and 112 ± 21 nm for the thiol capped and uncapped NPs, respectively (see ESI†).

Successful functionalization of NPs by thiol was assessed in several ways. ^{1}H NMR experiments were performed during the functionalization step by spraying NPs in a vessel containing deuterated acetone. The evolution of peaks relative to CH_2 groups in proportion to the NPs thiol function was followed as a function of time after addition of NPs (Fig. 3).

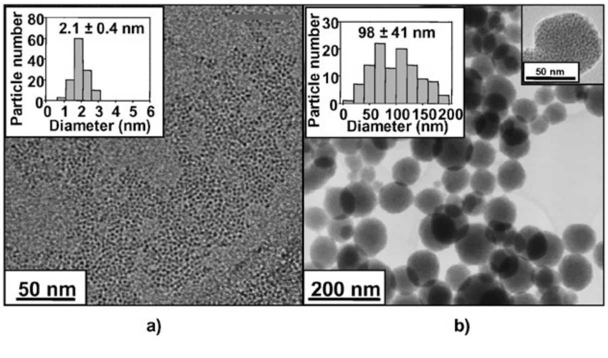

Fig. 2 TEM image and size distribution of palladium nanoparticles (a) functionalized by heptadecafluoro-1-decanethiol; (b) non-functionalized.

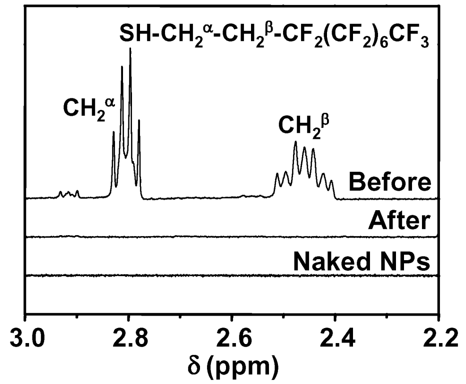

Fig. 3 ^{1}H NMR spectra showing the evolution of perfluorodecanethiol $CH_2{}^\alpha$ peaks before, after addition of palladium NPs and the spectrum of palladium NPs alone in deuterated acetone.

The disappearence of this peak (less than one hour in our conditions) demonstrated the grafting of thiol on the NPs. This was confirmed by solubilisation experiments. As expected, the perfluorodecanethiol capped NPs were easily dispersed in a perfluoro solvent (FC-72®) and remained stable over weeks, contrary to the uncapped NPs that are stable only for few hours.

To illustrate the versatility of our method and to produce colloids efficient for catalysis, we used ionic liquids (ILs) to stabilize our palladium NPs instead of thiols. ILs have received attention as alternative solvents and stabilizers for nanomaterials synthesis due to their stabilities (nonflammable, thermally stable) and low vapor pressures.[9] The use of these metal NPs for catalytic applications in the field of sustainable chemistry is of special interest.[10] However, the size control of the NPs is difficult to obtain: it necessitates the addition of a supplementary capping agent[11] or the careful choice of the IL.[12] The separation of growth and functionalization steps could therefore be a very useful strategy. In the literature the use of palladium NPs of average size 6 nm as catalysts for an Heck reaction has been described.[10] As already described for thiol capped NPs, palladium NPs of average size 2.1 ± 0.4 nm were formed after the growth of NPs in supercritical fluid. These palladium NPs of controlled size were brought to the functionalization vessel filled with $BMIMPF_6$ (1-*n*-butyl-3 methylimidazolium hexafluorophosphate), playing the role of solvent and functional agent. Due to its very low vapor pressure at ambient temperature, IL allows a complete removal of acetone by simple evaporation. TEM observations of the colloidal solution of $BMIMPF_6$ (that can be considered as *in situ* observations[10]) show palladium NPs with size and size distribution similar as those obtained with thiols (see ESI for TEM micrograph and size distribution†).

The catalytic efficiency of the $BMIMPF_6$ functionalized palladium NPs was tested with functional palladium NPs (1% in mass of reactive agents) using Heck reaction between iodobenzene (3 mmol) and styrene (3 mmol) using triethylamine as a base (Fig. 4, see ESI† for more experimental details). The turn over number (TON) was found to be equal to 2500 which is in good agreement with the catalytical activity

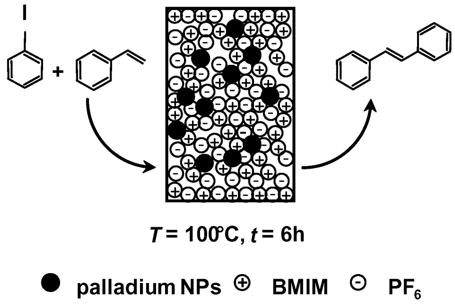

Fig. 4 Heck reaction of iodobenzene with styrene catalyzed by $BMIMPF_6$ functionalized palladium nanoparticles.

obtained with IL stabilized palladium NPs of average size of 6 nm in literature.[10] As in our case NPs are quite smaller (2 nm) and so have a larger surface available for the catalytical process, this result is in good agreement with the J. Dupont *et al.* paper that has demonstrated that the 6 nm NPs act only as reservoirs for smaller catalytical species. Lastly, both particles, thiol capped- and IL functionalized-NPs, were used as catalyst for the reaction of styrene with iodobenzene (Heck reaction) and only the $BMIMPF_6$ functionalized palladium NPs lead to the formation of stilbene. The catalytic surface of thiol capped palladium NPs is passivated by thiol that prevents any reaction taking place.

In conclusion, we have developed a new synthetic method to control core and shell properties of hybrid inorganic NPs. This method was successfully applied to the synthesis of palladium NPs capped with thiol or stabilized in IL and can be generalized for core and shells of different compositions and properties.

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