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Core-shell and homogenous distributions of functionalized cerium oxide nanoparticles were observed within spray-dried mesostructured silica spheres according to the templating agent in use.

In the past fifteen years a large number of studies has been focused on long-range ordered mesoporous materials obtained in solution through the self-assembly of a variety of amphiphilic templating agents with a growing inorganic phase¹. Recently, several works showed that their well known structural characteristics (high surface area, tunable geometry of the porous network, narrow pore size distribution)² are preserved and enhanced by mean of a spray drying process, which revealed to be interesting for its ease and possibility to obtain spherical particles. In ref. 2c, 3, experimental conditions as well as different structuring agents were successfully tested while in ref. 4 SAXS, TEM and mainly solid state NMR were used to better understand the process of particle and mesophase formation with time. As far as the last point is concerned, Boissière *et al.*⁵ used time-resolved in-situ SAXS to determine the required conditions for the mesophase to form. As far as applications are concerned, spherical shaping and possibility to embed maghemite nanoparticles within silica matrix readily showed an interest in applications like drug delivery and magnetic resonance imaging⁶ while calysis was rather explored in presence of Pd nanoparticles⁷ and nanowires⁸. In these cases, the way nanoparticles are located inside the silica particles is of primary importance according to the final application. For instance, in catalytic application, one could hope to enhance interactions between external fluids and embedded nanoparticles by placing them silica surface rather than in its bulk. In this way, diffusion paths are limited to the external crust. On the contrary, if nanoparticle delivery is the final objective, an homogenous distribution within the silica bulk would probably be the best solution.

For these reasons, we want to show the possibility to tune the spatial distribution of plain and functionalized cerium oxide nanoparticles inside spherical mesostructured silica particles produced by the spray-dried technique. The goal is double: firstly we would like to show some tricky interactions effects between functionalized nanoparticles and surfactants employed to structure

silica; secondly, we would like to open some perspectives as far as possibilities of easy controlling the spatial distribution of embedded nanoparticles.

Surface modifications of cerium oxide, CeO₂[‡], nanoparticles (used as received) was accomplished according to the procedure developed in ref. 9. Calculated ceria mass with respect to TEOS is about 10%. Surface modification is performed by addition of 5-phenyl phosphonic acid (PPA) and 3-amino propyl phosphonic acid. When PPA is used, homogenous dispersion of nanoparticles can only be obtained by addition of THF while no THF is employed with amino-propyl phosphonic acid. Ceria solution is then mixed with a CTAB (Cetyltrimethylammonium bromide - Aldrich) /water/HCl/Ethanol solution to which TEOS (tetraethoxysilane - Aldrich) is finally added. This is the spray-dried sol. Final mass (in grams) are the following:

CeO ₂	PPA	THF	TEOS
0.132	0.012	0.338	4.690
CTAB	EtOH	H ₂ O	HCl (μL)
1.480	30.460	15.890	3.6

Check of functionalization was performed by FT-IR spectroscopy for both amino and phenyl modified systems. Disappearing of FTIR bands of free P-O vibration at 2300 cm⁻¹ region and lack of free P=O band in the 1200 cm⁻¹ region (ESI) suggest a tridentate binding of phosphonate group. For the amino modification, additional peaks at 1047 and 1090 cm⁻¹ suggest the presence of asymmetric stretching vibrations of P-O as detected in PO₃²⁻ group, though C-N vibrations also resonate in this region. Unfortunately, these same vibrations are masked by the strong peak at 1070 cm⁻¹ and belonging to THF.

FT-IR gives a primary evidence of functionalization but exact mechanism and quantification is far from being determined, being this a very hard task to be put in evidence.¹⁰ Solution of functionalized cerium oxide nanoparticles is finally added to precursor sol mixture and eventually set in the spraying chamber. Experimental apparatus was described elsewhere^{2c}; here, we have set the drying chamber temperature to 150°C, the furnace temperature to 350°C while the relative humidity was set to 20%. X-ray diffraction (XRD) was performed in a θ-2θ geometry (Cu Kα, λ ~ 0.154 nm) (Philips PW 1820) while Transmission Electron Microscopy (TEM) was done on a Jeol 100 JX/STEM apparatus. Nitrogen adsorption/desorption isotherms were realized on a Micrometrics ASAP 2100 machine.

Figure 1 shows the X-ray diffraction patterns of as-synthesized mesostructured silica materials and in presence of amino-modified and phenyl-modified cerium oxide particles. All patterns are characteristics of a 2D-hexagonal mesophase, as shown by the (10),

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(11) and (20) reflections. Addition of the nanoparticles does not modify the long-range order within the material, both when hydrophilic and hydrophobic functions are used.

Fig. 1 X-ray diffraction patterns of spray-dried mesostructured silica particles embedding cerium oxide nanoparticles with (a) no functionalization, (b) amino functionalization and (c) phenyl functionalization.

A possibility exists that nanoparticles with hydrophobic functions are embedded within micelles but this is excluded by the nitrogen adsorption/desorption isotherms shown in Figure 2, where adsorbed volumes are of the order of 450 cm³/g in both calcined samples and BET surface areas range about 1100 m²/g. The capillary condensation occurs at values below P/P₀ = 0.4, as typically observed for CTAB-templated materials. In addition, no real difference in the isotherms is observed meaning that the presence of nanoparticles does not interfere with mesostructuring process.

Fig. 2 Adsorption/desorption isotherms of spray-dried mesostructured silica particles embedding cerium oxide nanoparticles with (a) no functionalization, (b) amino functionalization and (c) phenyl functionalization.

Electron microscopy images of all materials are shown in Figure 3. When no modification is performed (a,b), ceria nanoparticles are quite well dispersed throughout the mesostructured silica matrix though aggregation seem to occur in some particles areas. Nevertheless, no preferential site seem to be preferred by nanoceria to settle during the mesostructuring process. When the phenyl group is used as surface modifier, cerium oxide aggregates are also homogeneously dispersed within the silica matrix, as figure 3 (c,d) show. Dispersion is very similar to system without modification. When zooming out on figure 3 (e), an estimation of nanoaggregates dimension hands out values between 5 and 8 nm, which makes these objects too large to fit within CTAB templated pores, whose average pore diameter from N₂ adsorption/desorption data is 2.3 nm. Reasons of quite homogenous dispersion could be probably found in interactions between silica and functionalized nanoaggregates. An interesting discussion on silica surface chemistry on similar materials is lead by Alonso *et al.*^{4a}; they observe a high percentage of unreacted ethoxy groups when initial sols is not aged enough time, as it occurs in our case. For sake of truth, they could correlate good 2D-hexagonal order with low percentage of ethoxy groups. In our case, we observe very well ordered materials, which suggest rather well hydrolyzed TEOS. As far as hydroxy groups are concerned, they attributed the low OH NMR signal to both water and silanols. It is known that hydrophilicity of silica surface in mesostructured powders vary very much between very acidic and very basic conditions¹¹. Here, due to the mild initial pH and to the important presence of ethanol, it would be difficult to extrapolate a clear picture. Nevertheless, it would not be surprising that low percentages of silanols and adsorbed water combined to the existence of unreacted ethoxy groups may render an overall hydrophobicity of the material core. In addition, the homogeneously dispersed and generalized presence of CTAB could definitely contribute to exclude possible hydrophilic areas and enhance hydrophobic interaction with phenyl-functionalized cerium particles.

Fig. 3 Microtomed TEM images of mesostructured silica embedding (a,b) non-modified, (c-e) phenyl-modified and (f-h) amino-modified cerium oxide nanoparticles.

Figure 3 (f) shows the amino modified nanoaggregates embedded in mesostructured silica, where they prefer to set at the external silica/air interface. The localization of nanoparticles at the air/droplet interface was supposed and described before¹² (ref spalla 3). In their case, solvent evaporation rate was set to be the main parameter influencing the migration and aggregation of nanoparticle in a corona fashion. Parameters playing a crucial role seem to be the viscosity of the medium, evaporation rate of solvent and time needed to pass from liquid droplet to solid particle. In our system, all experimental conditions remain unchanged between non-functionalized and functionalized ceria embedding. The difference in the distribution behavior should be related to the presence of the amino function. Due to the fact that synthesis occurs at low pH, it is very likely that grafted amino groups are positively charged. Under these conditions, repulsion may take place between amino functions and positively charged amino headgroup belonging to CTAB surfactant micelles. Repulsion between positive charges may contribute to nanoparticle migration before consolidation of the silica network takes place in the oven. Verification of such an argument was tested by using neutral surfactants (results not shown), Brij58 and Pluronic P123 under the same synthesis conditions employed for CTAB. In any case a structured silica powder is obtained but surface modification did not influence at all the spatial distribution of ceria particles, which were always homogeneously distributed inside silica particles.

In conclusion, we propose a simple method to vary spatial distribution of functionalized nanoparticles within a mesostructured CTAB-templated silica sphere obtained by spray drying. When ceria nanoparticles are covered with hydrophobic functions or they are not functionalized at all, homogenous distribution is obtained. On the contrary, when an amino-containing function is introduced at low pH, migration towards the air/droplet interface is obtained.

Notes and references

[†] CeO₂ nanoparticles are obtained from the hydrate CeO₂(HNO₃)_{0.5}(H₂O)₄ delivered by Rhodia

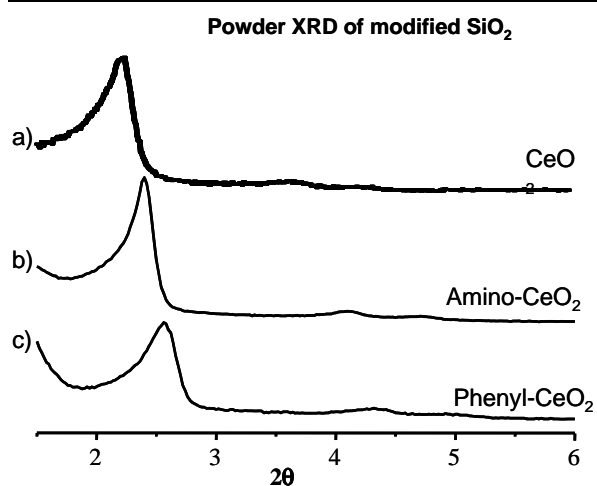


Figure 1

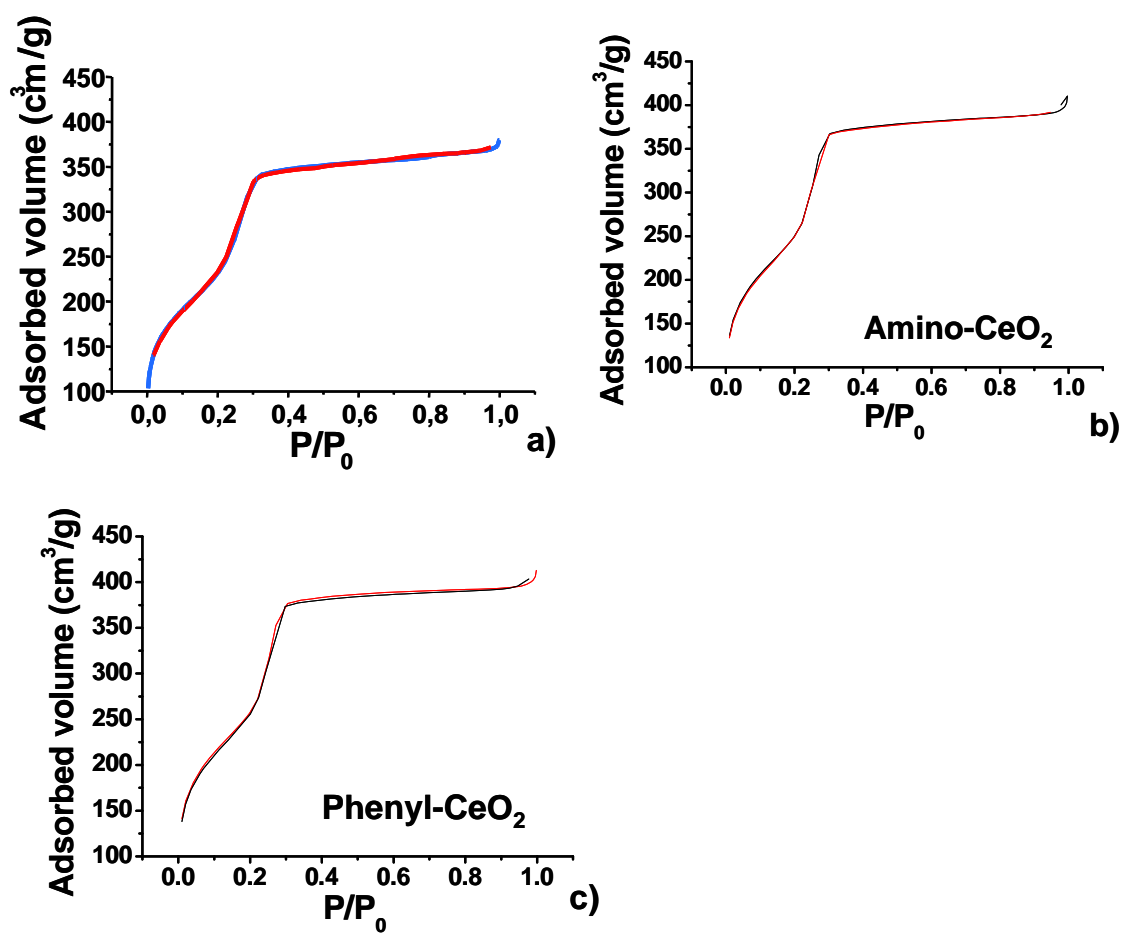


Figure 2

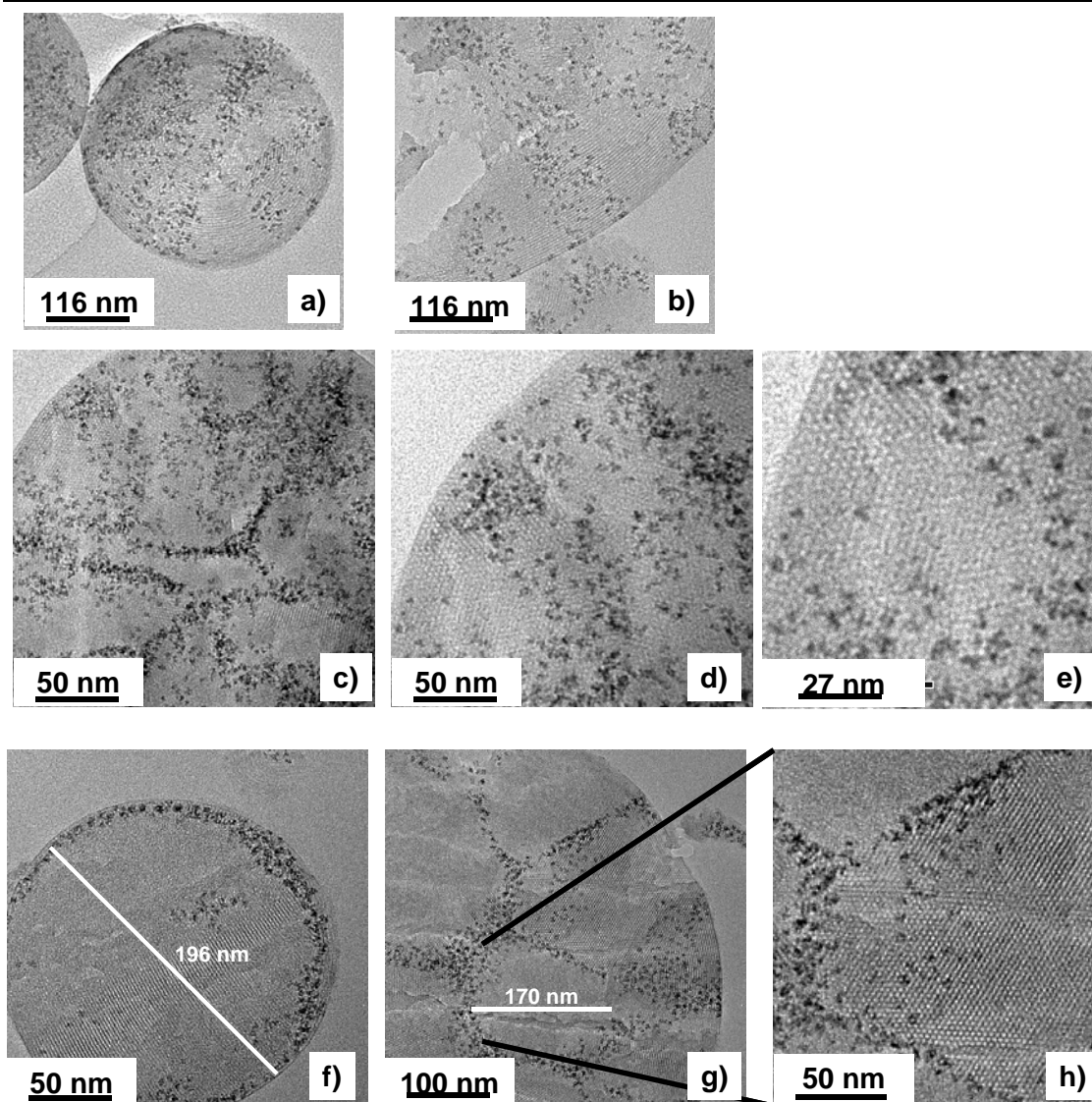


Figure 3

Supplementary Material (ESI) for Chemical Communications

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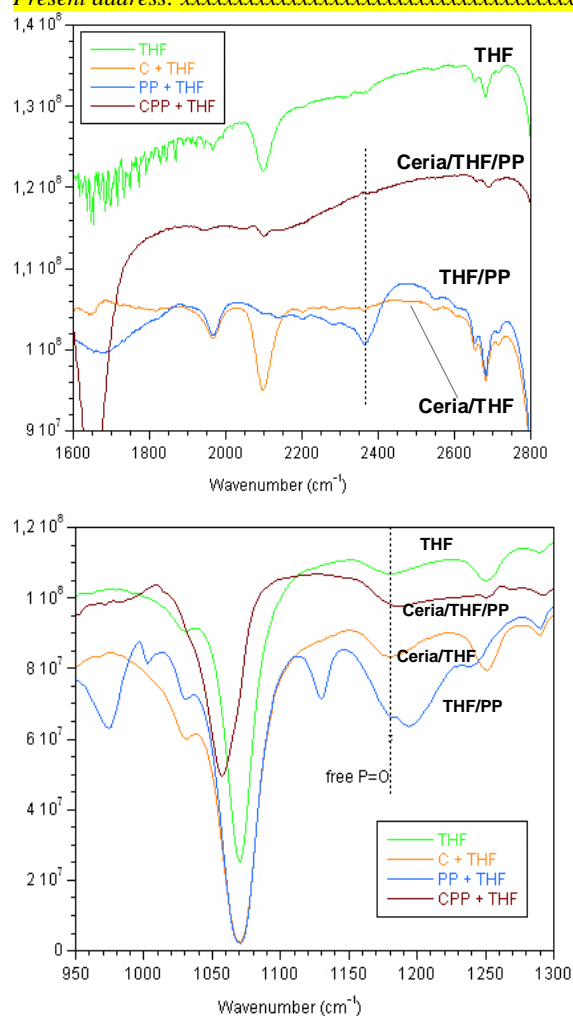
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The functionalisation of the nanoparticles is followed by FTIR spectroscopy. Disappearing of FTIR bands of free P-O vibration in the 2200-2300 cm⁻¹ region and lack of free P=O band in the 1200 cm⁻¹ region suggest a tridentate binding of phosphonate group. [see a) Botelho do Rego *et al.*, *Langmuir*, **2005**, 21, 8765; b) Bae *et al.*, *J. Phys. Chem. B*, **2004**, 108, 14093; c) Podstawka *et al.*, *Surf. Sci.*, **2005**, 599, 207; d) Lin-Vien *et al.*, *The handbook of IR and Raman characteristic frequencies of organic molecules*, **1991**, Academic Press, San Diego]

Fig. S1 FTIR spectrum of 5-phenyl-phosphonic acid (PPA) functionalised ceria nanoparticles in THF. For completion, THF, Ceria/THF and THF/PP spectra are shown.

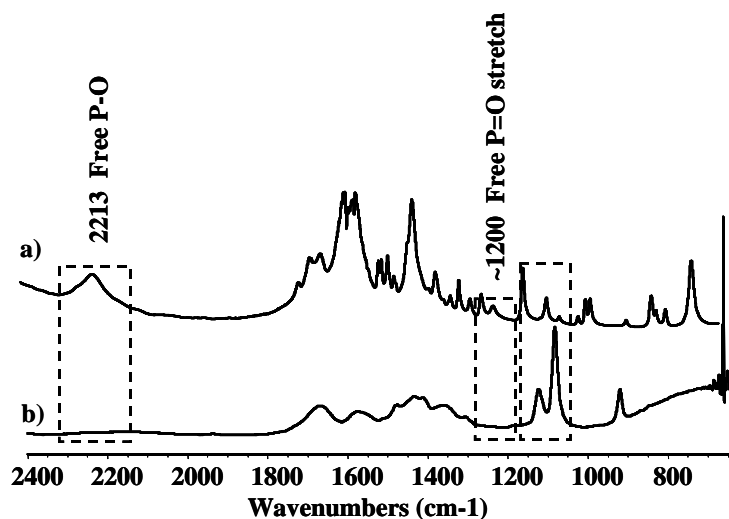


Fig.S2 FTIR spectra of a) 3-amino propyl phosphonic acid (PPA) and b) PPA functionalised ceria nanoparticles

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