A versatile method for the production of monodisperse spherical particles and hollow particles: Templating from binary core-shell structures†

Pablo Maximiliano Arnal,[a] Ferdi Schüth[a] and Freddy Kleitz[b]

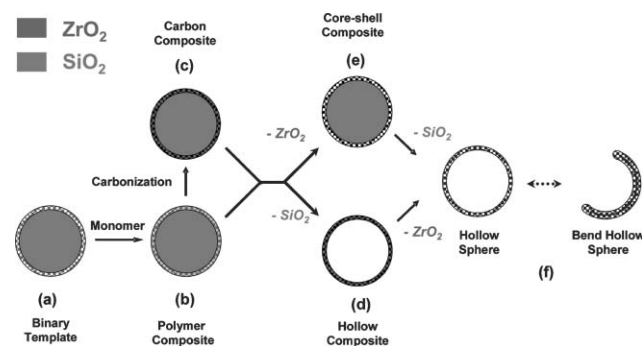**Using the porosity of a binary exotemplate, with mesoporous core-shell structure (SiO$_2$@ZrO$_2$), opens a new pathway to produce hybrid core-shell spheres, composite hollow spheres, and porous hollow spheres – all monodisperse in size.**

The formation of nanostructured composite materials by the combination of different inorganic and/or organic phases is highly promising for the generation of tailor made systems for applications in catalysis, optoelectronics, sensing, or biomaterials, among others. Such hybrid systems can exhibit new properties otherwise not available with only one of the phases, or allow the creation of multifunctional integrated systems.[1] Nanocasting methods employing hard inorganic templates are highly versatile in producing new porous materials, expanding the range of compositions available.[2] Particularly interesting for several applications are colloidal spherical core-shell systems with a monodisperse size distribution. These materials are ideal candidates for processes requiring an efficient mass transfer, for instance to improve electrolytes diffusion in solar cells,[3] or as drug carrier systems[4] and sensors.[6] Especially, the large pore volume in hollow composite spheres could act as a reservoir with a permeable barrier for controlling diffusion. To date, several methods of preparing porous core-shell systems have been proposed,[7] however, strategies enabling the fabrication of high quantities of monodisperse hybrid core-shell spheres remain highly challenging, a problem we are addressing with our nanocasting strategy.

In this communication, we demonstrate that the use of binary exotemplates (*i.e.*: exotemplate[2] with two material phases) provides an easy and general strategy for the synthesis of multicomponent nanoscale systems. The strategy is based on the use of a spherical core-shell structure (SiO$_2$@ZrO$_2$)[8] with high monodispersity in size, to synthesize hybrid core-shell spheres, composite hollow spheres and porous hollow spherical structures. The new type of binary core-shell template is easily obtained in large amounts, the details of the synthesis being reported elsewhere.[5] Such binary hard templates allow the preparation of different materials by replication of one or more of the components. The selective stepwise removal of the components of the exotemplate from the hybrid spheres provides new particle systems, where a new porous structure forms while the spherical morphology remains. The synthetic strategy is presented in

Scheme 1. The first step is the selective adsorption of a monomer (a precursor molecule for polymers or carbon) in the mesopores of the shell which surrounds the nonporous, inner core of the exotemplate (**a**). The impregnation of the monomers is performed in such a way that no organic species remain outside the shell, thus preventing eventual blocking of textural porosity between the colloidal spheres. Subsequently, the monomers are thermally polymerized in the confined space of the mesopores (**b**). In the case of carbogenic polymers, the polymer can be converted to carbon by high temperature treatment under either vacuum or an inert atmosphere (**c**). The composite sphere formed with either a polymer (**b**) or carbon (**c**) offers a starting point for a stepwise removal of the binary exotemplate. This may be done by two different routes each of which has two steps: one way is the removal of the exotemplate fraction of the shell to yield new core-shell (nonporous-porous) particles (**e**), which further continues with the removal of the core to obtain monodisperse hollow particles (**f**). The other pathway begins with the extraction of the core to provide a hollow composite sphere (**d**), followed by the removal of the exotemplate from the outer shell yielding a hollow structure with a porous shell (**f**).


Scheme 1 Synthetic strategy using a binary exotemplate.

To demonstrate the concept of multiple step nanocasting with a binary template, the porous outer shell of a binary exotemplate (SiO$_2$@ZrO$_2$) was filled with given amounts of furfuryl alcohol (monomer) and a polymerization catalyst (H$_2$C$_2$O$_4$)‡, as a first example. The polymerization is thermally triggered and, subsequently, polyfurfuryl alcohol is carbonized. Various core-shell and hollow spheres systems are then generated by using a controlled and stepwise dissolution of one or the other component of the exotemplate. The materials obtained at different steps in this new pathway were characterized by nitrogen physisorption at 77 K. The results of these analyses, shown in Fig. 1, reveal the evolution of the porosity in the different materials and changes in the specific surface area. Surface areas and pore volumes at the different steps are listed in Table 1. One should note the remarkable textural properties of the

[a] *Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470, Mülheim, Germany. E-mail: arnal@mpi-muelheim.mpg.de; schueth@mpi-muelheim.mpg.de; Fax: +49 0208-306 29 95; Tel: +49 0208 306 23 73*
[b] *Department of Chemistry, Université Laval, Québec, Canada. E-mail: freddy.kleitz@chm.ulaval.ca; Fax: + 1 418 656 7916; Tel: +1 418 656 7812*
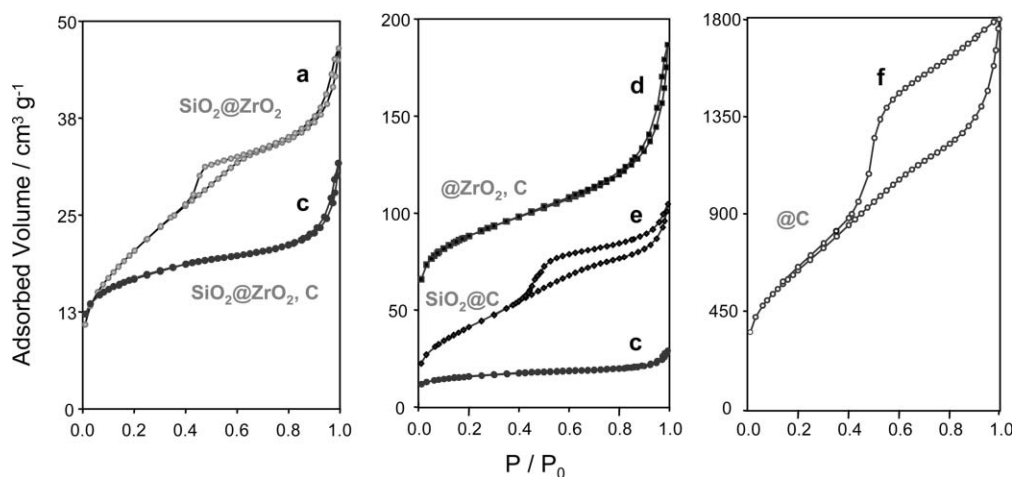
Fig. 1 Nitrogen sorption isotherms for the exotemplate (**a**), SiO$_2$@ZrO$_2$,C (**c**), @ZrO$_2$,C (**d**), SiO$_2$@C (**e**), and @C (**f**).

final carbon sample. The exotemplate (SiO$_2$@ZrO$_2$) (**a**) presents a type IV isotherm, characteristic of mesoporous materials. The capillary condensation step visible at P/P$_0$ around 0.5 with pronounced hysteresis loop reflects the mesoporosity in the shell and in voids present between the shell and the silica core. Detailed characterization of this template material can be found elsewhere.[5] The filling of the porous structure in the shell with carbon yields the material denoted SiO$_2$@ZrO$_2$,C (**c**). Its isotherm evidences clearly the filling of the mesopores with the reduction of the slope of the adsorption branch and in the loss of the hysteresis loop. The isotherm changes to approximate a type I. However, the non zero slope in the multilayer region of the isotherm indicates the presence of residual mesopores. Importantly, the secondary mesoporosity observed at high relative pressures which is assigned to porosity among the colloidal spheres is retained for SiO$_2$@ZrO$_2$,C. From these composite core-shell spheres (**c**) two distinct pathways are possible for a step-wise removal of the inorganic exotemplate. First, the composite spheres can be treated with an aqueous solution of NaOH 1 N to selectively remove the siliceous core generating hollow composite spheres (**d**) (Fig. 2). It is assumed that the transport of matter from the interior to the exterior of the core-shell particles is made possible through remaining porosity in the composite shell. The obtained composite hollow spheres (**d**) show an isotherm similar to the isotherm of (**c**), but displaced upwards. This effect is due to the loss of silica, which contributes significantly to the mass of the particles but little to the specific surface area. The composite hollow spheres can then be converted to hollow carbon spheres (**f**) if treated with aqueous HF solution. Thus, a porous structure forms in the shell during the removal of ZrO$_2$. These changes are reflected in the reappearance of the hysteresis and in the increase of adsorption capacity with upwards displacement of the isotherm.
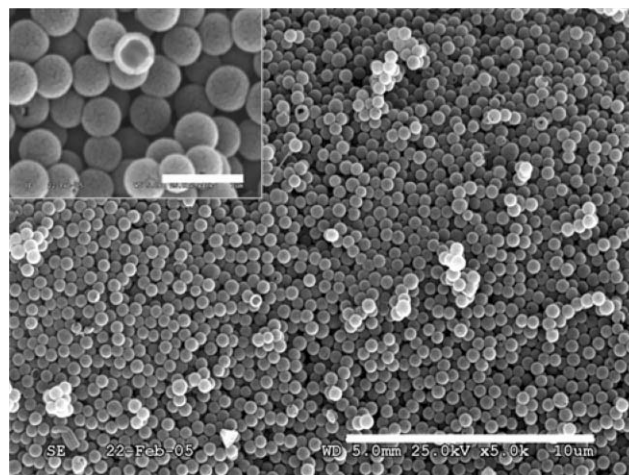
In the second way, the hybrid core-shell spheres (**c**) can be transformed into core-shell particles without ZrO$_2$ at the shell (**e**) by a treatment with stoichiometric amounts of HF. The resulting SiO$_2$@C spheres reflect the formation of a new porous structure as expressed by the isotherm shown in Fig. 1, with capillary condensation step and hysteresis loop in relative pressure ranges corresponding to mesopores. Since tetragonal ZrO$_2$ forming the shell is much denser than amorphous silica and carbon, the spheres lose substantial mass resulting in an upwards displacement of the isotherm, similarly to the step (**d**) → (**f**), while mesopores form. The core-shell spheres (**e**) can be transformed into hollow spheroids (**f**), if the core is dissolved either by an alkaline (NaOH) solution or by an acidic (HF) solution. The final @C particles exhibit the same morphology irrespective of the sequence adopted for the removal of the binary template.

EDX analyses of the materials at different stages confirm the stepwise removal of the exotemplate. For the sample (**d**), the Si content is drastically reduced, but silicon is still detected, because a fraction of silicon is included with the ZrO$_2$.[5] For (**e**) a complete removal of Zr indicates the dissolution of the ZrO$_2$ from the shell. Finally, in the case of (**f**) neither silicon nor zirconium is observed. This indicates the efficient and consecutive removal of the different components of the exotemplate. Furthermore, the distribution of
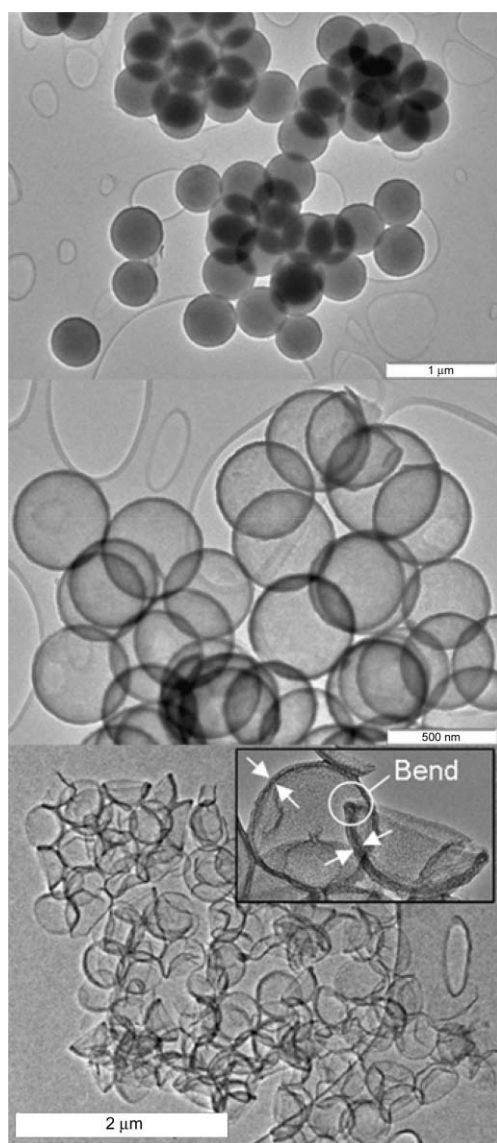
Table 1 Textural parameters and EDX analysis at different steps

Sample	Surface area[a]/ m^2 g^{-1}	Pore volume[b]/ cm^3 g^{-1}	Elemental composition[c]				
			Si	Zr	C	O	Na
(**a**)	75	0.064	31	2	0	67	0
(**c**)	54	0.038	—	—	—	—	—
(**d**)	304	0.24	6	7	52	33	2
(**e**)	151	0.14	28	0	26	46	0
(**f**)	2343	2.4	0	0	93	7	0

[a] BET method. [b] At P/P$_0$ = 0.97. [c] Percentual (atomic).

Fig. 2 SEM image of @ZrO$_2$,C. Scale bar 10 μm and 1 μm (inset).

carbon species was shown to be homogenous around the shell as evidenced by line scan experiments of the spheres with EDX (results not shown).

The colloidal core-shell particles were imaged during the different steps of the mutiple-step casting pathway using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). During these investigations, no carbon outside the porous structure of the spherical particles could be detected (Fig. 2). Furthermore, the spheres do not cross-link or agglomerate, and mostly isolated core-shell spherical particles are produced. Detailed TEM investigations (Fig. 3 and ESI Fig. S1) of a $SiO_2@ZrO_2,C$ illustrate the efficient pore filling of the zirconia shell, with trace amounts of carbon formed as a coating around the shell when high loadings of furfuryl alcohol are used. After removal of one component of the binary exotemplate, the spherical morphology is retained suggesting homogeneous filling.

Mesoporous hollow carbon spheres are obtained after complete template removal. A substantial fraction of these particles are deformed, probably due to their mechanical properties, resulting in bend spheres (Fig. 3 bottom). Such bend particles have been observed before in the case of other hollow spheres.[9] In Fig. 3 (bottom, inset) we can see both a well defined sphere and a cup-like folded particle, the latter having a wall thickness twice as high as the former, which is a result of the two hemispheres collapsing onto each other.[10] Moreover, the bend in the cup-like particle clearly shows that it had formed from a sphere which bent. One should note that in SEM images, most of the spheres appear cup-shaped, probably due to the different sample preparation.

This strategy is being extended to produce different core-shell and capsule structures with a wide variety of organic species, which may be integrated in the shell of the binary template, and so far the results seem to converge. For example, organic polymers such as polymethacrylic acid (PMAA) and polymethyl methacrylate (PMMA) can be introduced into the pores in the shell following a similar selective positioning of monomers inside the mesopores. The vinyl monomers could be subsequently polymerized in the shell to yield organic–inorganic hybrid core-shell spheres. (See ESI Fig. S2 and S3). These results confirmed that we were able to introduce selectively organic precursors within the mesoporous shell of a binary template with core-shell structure and to restrict their polymerization in the confined space of the porous shell. The different chemical behavior of typical carbon precursors and vinyl monomers points to a broad applicability of the proposed procedure for the generation of functional monodisperse core-shell particles.

In conclusion, we have introduced the use of a binary exotemplating system, as a versatile method of manufacturing composite core-shell spheres and hollow capsules – all remaining monodisperse in size – which are interesting candidates to be further surface functionalized.[11–13]

Notes and references

‡ The synthesis of the materials is described in detail in the ESI.

1 (a) C. Sanchez, B. Lebeau, F. Chaput and J. P. Boilot, *Adv. Mater.*, 2003, **15**, 1969; (b) C. Sanchez, B. Julian, P. Belleville and M. Popall, *J. Mater. Chem.*, 2005, **15**, 3559.
2 F. Schüth, *Angew. Chem., Int. Ed.*, 2003, **42**, 3604.
3 A. Hagfeldt and M. Grätzel, *Chem. Rev.*, 1995, **95**, 49.
4 Y. Zhu, J. Shi, W. Shen, X. Dong, J. Feng, M. Ruan and Y. Li, *Angew. Chem., Int. Ed.*, 2005, **44**, 5083.
5 P. M. Arnal, C. Weidenthaler and F. Schüth, *Chem. Mater.*, submitted.
6 L. M. Liz-Marzán, M. A. Correa-Duarte, I. Pastoriza-Santos, P. Mulvaney, T. Ung, M. Giersig and N. A. Kotov, in *Handbook of Surfaces and Interfaces of Materials*, ed. H. S. Nalwa, Academic Press, San Diego, 2001, Vol. 3, ch. 5.
7 K. Moller, T. Bein and R. X. Fischer, *Chem. Mater.*, 1998, **10**, 1841.
8 For clarity, we use a nomenclature for the core-shell particles similar to that commonly employed for metal-doped buckminsterfullerenes: core@shell systems.[6] For a shell with more than one component, materials are denoted core@A,B, … ,M.
9 X. Xu and S. A. Asher, *J. Am. Chem. Soc.*, 2004, **126**, 7940–7945.
10 The rigidity of the final @C particles increases with the initial furfuryl alcohol loading.
11 H. P. Boehm, *Carbon*, 1994, **32**, 759.
12 (a) C. A. McNamara, M. J. Dixon and M. Bradley, *Chem. Rev.*, 2002, **102**, 3275; (b) M. Benaglia, A. Puglisi and F. Cozzi, *Chem. Rev.*, 2003, **103**, 3401.
13 M. Choi, F. Kleitz, D. Liu, H. Y. Lee, W.-S. Ahn and R. Ryoo, *J. Am. Chem. Soc.*, 2005, **127**, 1924.

Fig. 3   TEM-images of $SiO_2@ZrO_2,C$ (top), $@ZrO_2,C$ (middle) and $@C$ (bottom).