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Hierarchically porous nanostructures through phosphonate-metal alkoxide condensation and growth using functionalized dendrimeric building blocks[†]

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Controlled titanium alkoxide mineralization in the presence of phosphonated, dendrimeric nano-building blocks provides a new family of hierarchically porous dendrimer-bridged titanium dioxide materials.

The strategic development of rationally designed, multifunctional, architectural materials lies at the forefront of the field of material synthesis.¹ Of particular interest is that the nano-scale association of soft and hard matter in the same building blocks by the so-called self-assembly process² provides access to exciting nanohybrids with synergetic inorganic– organic properties such as thermal and structural stability (from the inorganic matrix) and specific functional group reactivity (from the organic fragment).

There are various synthetic pathways to generate hybrid materials, which span from conventional sol-gel polymerisation to more sophisticated coating and self-assembly techniques, intercalation, nano-replication and casting, pillaring and exfoliation.³ The crucial challenge in the synthesis of these nanostructured materials concerns the necessary use of a sacrificial template in order to generate ordered porous networks.⁴ Such nanostructures are used in a variety of applications as, for example, adsorbents, sensors and indicators, drug delivery systems, or as heterogeneous catalysts. Unfortunately, the difficulties associated with the costly synthesis of the lyotropic templates and environmental concerns associated with their removal overwhelm the real benefits of these materials. There is therefore a real need for sustainable and less energy-intensive synthetic protocols to produce multifunctional hybrid materials featuring hierarchical substructures.5

Here, we present an alternative strategy for making porous organic-inorganic multifunctional hybrid materials, in a one-pot synthesis by condensation between a branched dendrimer and an inorganic alkoxide monomer. This route takes advantage of the well-controlled topology of the rationally designed phosphorus dendrimers⁶ in terms of their organisation on the nanoscale, their nanoporous cavities, their compacted hydrodynamic volume in solution, their controlled dispersion and the large density of functional groups at the peripheral branches.⁷ With this aim, the external surface of the dendrimers has been functionalized with phosphonic acid salts that form a strong covalent bond with transition metals (P-O-M: $M = Ti, Zr, Al)^8$ as demonstrated during the post-grafting of hybrid material.^{9,10} Herein, the targeted dendrimers were designed to cross-link metal alkoxides and to template mineral growth from the processable sol-gel monomers.

Three generations of phosphonated dendrimers (G_2 , G_3 and G_4) have been utilized in this study (Fig. 1 and S1, ESI†). Titanium tetraisopropoxide, Ti(O*i*Pr)₄, has been selected as the inorganic source, ethanol as the solvent and water as the catalyst.

In a typical procedure for the material synthesis, a phosphonated dendrimer was solubilised in an ethanol/water (5/2 v/v) solution. After 15 minutes of stirring, a titanium alkoxide precursor in a given molar ratio ([dendrimer]:[Ti] = 1:5, 1:10 or 1:20) was added to the transparent dendritic solution at room temperature. Upon addition, the solution became cloudy through polymerisation of the titanium precursor and the resulting solution was heated at 60 °C for 10 hours. After filtration and extensive washing of the precipitate with ethanol, the collected solid was dried at 60 °C for 2 hours. Hereafter, the materials are denoted M–G_x–*R* (where *x* refers to the dendrimer generation (2, 3 or 4) and *R* is the dendrimer: Ti ratio used (1:5, 1:10 or 1:20)).



Fig. 1 Dendrimer G₄.

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The structural properties of these materials were elucidated by means of CP MAS NMR and DRIFT analysis. ¹³C CP MAS NMR clearly shows the characteristic signals of the organic skeleton at 33, 46, 55 and 72 ppm and those of the aromatic rings at 122, 130, 139 and 150 ppm, which indicate the preservation of the dendritic structure during the sol-gel polymerization (see ESI[†], S2). The ³¹P MAS NMR spectra of the solid materials exhibit signals characteristic of the parent dendrimers-in particular, those corresponding to the cyclophosphazene core at 5 ppm, internal phosphorus at 65 ppm and peripheral phosphonate groups at 18 ppm (see ESI⁺, S3). Compared to the native dendrimers, the broadness of the signals for the phosphonic groups in the hybrid materials indicates the significantly reduced mobility of the peripheral fragments, which is consistent with their covalent bonding to the titania network.^{9,11} DRIFT analysis revealed signals characteristic of the dendritic substructures (see ESI⁺, S4). The disappearance of the absorption peak at 910 $\rm cm^{-1}$ assigned to the phosphonate P-OH and the merging new bands at 1080 cm⁻¹ (due to the P-O···Ti stretching vibrations) provide evidence for extensive condensation between the titanium alkoxide and the phosphonate groups of the dendritic structures to form bridged P-O-Ti hybrid materials.9-11

The textural properties of these hybrid materials were investigated using scanning and transmission electron microscopy techniques (SEM and TEM, respectively), X-ray diffraction analysis and nitrogen sorption measurements. As evidenced by SEM micrographs, the network of the materials is composed of spherical particles connected to each other to form a continuous network. The size of the spheres varies slightly within the series of the materials from 100 to 150 nm (see Fig. 2a and S5, ESI†). TEM provides useful information concerning the organization on the nano-scale of these crosslinked dendritic networks. Interestingly, small particles seem to be well entangled in the network of the material and no bulk material or separated phase was observed. Disordered mesopores (intercrystalline pores) are abundant throughout



Fig. 2 (a) SEM image of the hybrid dendrimer-titania material $(M-G_2-1:10)$. (b) Comparison of the nitrogen physisorption isotherms of $M-G_x-1:20$ (x = 2, 3, 4). (c) TEM image showing the crystalline anatase planes in the hybrid material $(M-G_2-1:10)$. (d) SAED showing the planes of titania anatase.

the microstructure. At higher magnification, the individual crystals (~ 5 nm in width) of anatase TiO₂ are clearly observed. The HRTEM image allows for the resolution of lattice fringes of the crystals assigned to the {101} planes of the anatase titania (Fig. 2c and d and S6 in ESI⁺). The calculated interplanar distance is 3.5 Å, which is in line with the results obtained from the X-ray diffraction patterns. The XRD pattern exhibits peaks that can be assigned to the anatase phase of the titanium dioxide (ESI⁺, S7). The size of the nanocrystals estimated from the half-height width of the {101} peak using the Scherrer formula corresponds to the average crystallite size ranging from 4 to 7 nm, in accordance with the results obtained from TEM analysis. The nanocrystals are homogeneous in their composition as evidenced by local mapping of the distribution of titanium dioxide in the hollow network by EDX analyses (ESI[†], S8). In three different zones, the same Ti/P (or S) ratio (P and S from the dendrimer) was found, which excludes the formation of core-shell structures and unambiguously precludes the formation of two phaseseparated heterogeneous zones. Moreover, this highlights the pivotal role played by the dendrimer substructures as anchoring points for the nucleation and further mineral growth of the nanocrystalline titanium dioxide.¹²

The texture of the solid network of these hybrid materials was further investigated by nitrogen sorption analysis. Regardless of the generation of the dendrimer and the [dendrimer]: [Ti(OiPr)₄] ratio used, the materials displayed high porosity with surface areas ranging from 203 to 514 m² g⁻¹ (Table 1). Although the surface area decreased significantly after increasing the ratio from 1:5 to 1:20, the mesoporous network became more pronounced, as evidenced by the appearance of hysteresis in the adsorption–desorption isotherm (Fig. 2b and S9 in ESI[†]).

The porosity observed in native hybrid dendrimer– TiO_2 (*i.e.* without calcination) is quite surprising. When the native, unmodified dendrimer networks are assessed by nitrogen adsorption, these solid materials present virtually no porosity indicative of a densely packed dendrimer network. It is well known that such substructures present an open-framework when solvated because of their excellent swelling capacity;⁷ the internal voids of these stiff nanoscale macromolecules being as the basis of their use as hosts for small guests and for the encapsulation of biomolecules.¹³ The entropic effect due to the presence of a solvent keeps the dendrimer strands separated in

Table 1 Textural properties of dendrimer-titania hybrid materials

Entry	Material	Particle size ^{<i>a</i>} /nm	$\frac{S_{\rm BET}}{\rm m^2~g^{-1}}^{b/}$	$\frac{V_{\mathrm{meso}}^{}b}}{\mathrm{mL~g}^{-1}}$	$D^{b,c}/$ nm
1	$M-G_2-1:5$	$5(5)^d$	511	0.11	2.98
2	$M-G_2-1:10$	6.4	356	0.25	3.86
3	$M - G_2 - 1 : 20$	4.9	386	0.2	3.12
4	$M - G_{3} - 1 : 5$	_	514	0.24	3.5
5	$M - G_3 - 1 : 10$	4	289	0.21	3.7
6	$M - G_3 - 1 : 20$	4.5	291	0.23	3.7
7	$M - G_4 - 1 : 5$	$5.8(5)^d$	456	0.17	3.3
8	$M - G_4 - 1 : 10$	7	361	0.2	2.8
9	$M - G_4 - 1 : 20$	4.4	203	0.2	3.12

^{*a*} From XRD. ^{*b*} From nitrogen sorption analysis. ^{*c*} From the adsorption branch using the BJH method. ^{*d*} From TEM.



Fig. 3 Schematic illustration of the material design: (i) coordination between the titanium alkoxides and phosphonate ligands, leading to the formation of reactive building blocks; (ii) cross-linking of the titanium alkoxides and further densification of the titania network; (iii) fusing of the elemental grains to form a continuous network.

their solvated state. However, upon drying, the dendritic branches are compliant enough to be drawn together by capillary forces. By sharp contrast, the results presented herein suggest that cross-linking of these objects provides a robust hydrogel network that can better withstand the tension of a receding solvent meniscus during drying.¹⁴ Thus, in solid state, the materials exhibit significant accessible porosity (Fig. 3).

From a mechanistic viewpoint, it seems that the initial step for material growth involves chelation of the metal alkoxide by the phosphonate ligands, which leads to strong connectivity between the organic and inorganic domains.¹⁵ This constitutes the primary reactive building blocks for material nucleation. The complexation of titanium alkoxide by phosphonate ligands decreases the reactivity of the metal and allows for more controlled condensation.¹⁶ The remaining alkoxy ligands bridged to titanium centers interact by hydrolysis–condensation, allowing for the continued formation and densification of the elemental grains. The process of condensation consumes the excess titanium alkoxide monomers by anchoring them to the growing structure and mitigates random aggregate formation. As the process goes on, the grains react with each other leading to the spherical network observed by SEM.

The thermal stability of these materials has been examined by thermogravimetric analysis (TGA) (S10 in ESI[†]). Thanks to the high stability of phosphorus dendrimers,¹⁷ only 20% of the skeleton degrades with heating. The preservation of the crystalline anatase (even after thermal treatment at 800 °C with a slight increase in the crystal size to ~9 nm) demonstrates the remarkable stability of the dendritic framework (S11 in ESI[†]). Surprisingly, no transformation to the brookite or rutile phase, commonly observed at this temperature range, has been detected.¹⁸ These important outcomes are mainly due to the steric hindrance of the dendritic skeleton, which hampers the thermodynamically favored phase transformation of the crystalline structure.

In summary, an efficient strategy to draw nonporous packed dendritic structures into the realm of stable porous hybrid materials has been validated by cross-linking their periphery with nanocrystalline titanium dioxide clusters. This strategy further provides interesting hierarchical materials in which photoactive crystalline anatase¹⁹ is grown in dendritic substructures. This hierarchical porosity, the photoactivity of the titanium anatase and the intrinsic properties of phosphorus dendrimers are likely to provide synergetic materials with advanced properties. This work is currently in progress in our laboratories.

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Notes and references

- 1 C. Sanchez, G. J. A. A. Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer and V. Cabuil, *Chem. Mater.*, 2001, **13**, 3061–3083.
- 2 G. M. Whitesides and B. Grzybowski, *Science*, 2002, 295, 2418–2421; I. W. Hamley, *Angew. Chem., Int. Ed.*, 2003, 42, 1692–1712; S. Mann, *Nat. Mater.*, 2009, 8, 781–792.
- 3 F. Hoffmann, M. Cornelius, J. Morell and M. Froba, Angew. Chem., Int. Ed., 2006, 45, 3216–3251; Y. Wan and D. Y. Zhao, Chem. Rev., 2007, 107, 2821–2860.
- 4 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710–712; D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548–552.
- N. Baccile, J. Reboul, B. Blanc, B. Coq, P. Lacroix-Desmazes, M. In and C. Gerardin, *Angew. Chem., Int. Ed.*, 2008, 47, 8433–8437; A. El Kadib, K. Molvinger, T. Cacciaguerra, M. Bousmina and D. Brunel, *Microporous Mesoporous Mater.*, 2011, 142, 301–307.
- 6 Review: J. P. Majoral and A. M. Caminade, *Chem. Rev.*, 1999, 99, 845–880; A. M. Caminade and J. P. Majoral, *Acc. Chem. Res.*, 2004, 37, 341–348.
- 7 J. Leclaire, Y. Coppel, A. M. Caminade and J. P. Majoral, J. Am. Chem. Soc., 2004, 126, 2304–2305; J. Jimenez, A. Laguna, A. M. Molter, J. L. Serrano, J. Barbera and L. Oriol, Chem.-Eur. J., 2011, 17, 1029–1039; P. Carbone and L. Lue, Macromolecules, 2010, 43, 9191–9197.
- 8 X. Tang, N. Yao and M. E. Thompson, *Supramol. Sci.*, 1997, 4, 35–42; G. Alberti, U. Costantino, C. Dionigi, S. Murciamascaros and R. Vivani, *Supramol. Chem.*, 1995, 6, 29–40; A. Clearfield, *Prog. Inorg. Chem.*, 1998, 47, 371–510.
- W. Gao, L. Dickinson, C. Grozinger, F. G. Morin and L. Reven, Langmuir, 1996, 12, 6429–6435; P. H. Mutin, G. Guerrero and A. Vioux, J. Mater. Chem., 2005, 15, 3761–3768; E. M. Ferrero, G. Franc, S. Mazères, C. O. Turrin, C. Boissière, A. M. Caminade, J. P. Majoral and C. Sanchez, Chem.–Eur. J., 2008, 14, 7658–7669.
- 10 X. J. Zhang, T. Y. Ma and Z. Y. Yuan, J. Mater. Chem., 2008, 18, 2003–2010; T.-Y. Ma, X.-Z. Lin and Z. Y. Yuan, Chem.–Eur. J., 2010, 16, 8487–8494.
- 11 M. N. Tchoul, S. P. Fillery, H. Koerner, L. F. Drummy, F. T. Oyerokun, P. A. Mirau, M. F. Durstock and R. A. Vaia, *Chem. Mater.*, 2010, **22**, 1749–1759.
- 12 G. J. A. A. Soler-Illia, L. Rozes, M. K. Boggiano, C. Sanchez, C. O. Turrin, A. M. Caminade and J. P. Majoral, *Angew. Chem.*, *Int. Ed.*, 2000, **39**, 4249–4254; G. Franc, E. Badetti, V. Collière, J. P. Majoral, R. M. Sebastian and A. M. Caminade, *Nanoscale*, 2009, **1**, 233–237.
- 13 D. Astruc, E. Boisselier and C. Ornelas, *Chem. Rev.*, 2010, **110**, 1857–1959; R. M. Crooks, M. Zhao, L. Sun, V. Chechik and L. K. Yeung, *Acc. Chem. Res.*, 2001, **34**, 181–190.
- 14 A. Bouchara, L. Rozes, G. J. A. A. Soler-Illia, C. Sanchez, C. O. Turrin, A. M. Caminade and J. P. Majoral, J. Sol-Gel Sci. Technol., 2003, 26, 629–633.
- 15 J. R. Errington, J. Ridland, K. J. Willett, W. Clegg, R. A. Coxall and S. L. Heath, J. Organomet. Chem., 1998, 550, 473–476; M. Mehring, G. Guerrero, F. Dahan, P. H. Mutin and A. Vioux, Inorg. Chem., 2000, 39, 3325–3332.
- 16 C. Sanchez, J. Livage, M. Henry and F. Babonneau, J. Non-Cryst. Solids, 1988, 100, 65–76; A. Léaustic, F. Babonneau and J. Livage, Chem. Mater., 1989, 1, 240–252; A. El Kadib, K. Molvinger, C. Guimon, F. Quignard and D. Brunel, Chem. Mater., 2008, 20, 2198–2204.
- 17 C. O. Turrin, V. Maraval, J. Leclaire, E. Dantras, C. Lacabanne, A. M. Caminade and J. P. Majoral, *Tetrahedron*, 2003, **59**, 3965–3973.
- 18 X. Chen and S. S. Mao, Chem. Rev., 2007, 107, 2891-2959.
- 19 A. Primo, A. Corma and H. Garcia, Phys. Chem. Chem. Phys., 2011, 13, 886–910.