View Article Online / Journal Homepage / Table of Contents for this issue

Mesoscopically ordered organosilica and carbon–silica hybrids with uniform morphology by surfactant-assisted self-assembly of organo bis-silanetriols†

Jiebin Pang,[ad] Lu Yang,[a] Douglas A. Loy,[b] Huisheng Peng,[a] Henry S. Ashbaugh,[a] Joel Mague,[c] C. Jeffrey Brinker[d] and Yunfeng Lu*[a]

Received (in Berkeley, CA, USA) 29th November 2005, Accepted 6th February 2006
First published as an Advance Article on the web 28th February 2006
DOI: 10.1039/b516985b

Published on 28 February 2006 on http://pubs.rsc.org | doi:10.1039/B516985B
Downloaded by Fudan University on 01 December 2012

Long-range molecularly ordered organosilica and carbon–silica hybrids with uniform morphology have been synthesized by surfactant-assisted hydrolysis and self-assembly of biphenyl bridged organosilane, followed by thermal polycondensation and carbonization.

Self-organization of organic and inorganic components over multiple length scales represents a significant approach towards sophisticated materials with spatially defined structures and functionalities for a wide spectrum of applications.[1,2] Bridged silsesquioxanes, a class of molecular building blocks defined as $(RO)_3Si–R'–Si(OR)_3$, where OR is a hydrolysable alkoxy group and R′ is a non-hydrolysable bridging functional group, hold great promise towards the synthesis of such materials.[1–10] To date, mesoscopically ordered hybrids from silsesquioxanes containing bridging units like bis-propylureido azobenzene,[11] giant diureido derivatives[2,12–15] and perylenediimide[16] show interesting morphologies and unique responsive and optical properties. The long-range self-organization of these bridged silsesquioxanes is driven by enhanced intermolecular interactions, in particular, strong π–π stacking from their conjugated bridging components. Although silsesquioxane precursors containing short conjugated groups (*e.g.*, phenyl, biphenyl) afford the anisotropic organization of organosilica hybrid networks, driven by the relatively weaker interactions between the aromatic bridging groups,[8,9] the reported hybrids were amorphous[8,9] and the long-range molecular ordering of these organosilica hybrids remains challenging. Solid-state hydrolysis/polycondensation of a crystalline bridged organosilane precursor[17] and thermal polycondensation of a crystalline bridged organo bis-silanetriol precursor[18] have been used to achieve these kinds of materials. Very recently, two research groups independently reported the synthesis of aromatic-silica hybrid materials, with molecular ordering achieved by controlling the hydrolysis and condensation reactions of aromatic organosilanes in basic and acidic aqueous solutions.[19,20] However, they either showed low yield (*e.g.*, 30–40%),[20] or showed broad and weak Bragg diffractions,[19] and the reported surface areas (*e.g.*, 200 m^2 g^{-1})[19] suggested the molecules were not closely packed to form a dense hybrid network. Importantly, all these reported materials[17–20] lacked uniform morphology control.

In this work, we report the synthesis of an organosilica hybrid material with high long-range molecular ordering and a uniform particle morphology. Interestingly, carbonization of the hybrid preserves the morphology, forming the first example of a molecularly-ordered carbon–silica hybrid material. The synthesis was achieved by thermal polycondensation and carbonization of self-assembled organo bis-silanetriols in the presence of a Pluronic surfactant (Pluronic-P123). The presence of P123 is critical in obtaining the high yield and uniform crystals due to it assisting with the dispersion of the hydrophobic precursors in water. This work also provides some insights towards a fundamental understanding of the self-assembly and co-assembly of bridged organosilicates in the presence of surfactant.

In a typical synthesis, 1.0 g of P123 ($HO(CH_2CH_2O)_{20}$-$(CH_2CH[CH_3]O)_{70}(CH_2CH_2O)_{20}H$, BASF product) was dissolved in 36 g of de-ionized H_2O and 1 mL of 37 wt% concentrated HCl. Next, 0.55 mL (1.2 mmol) of 4,4′-bis(triethoxysilyl)-1,1′-biphenyl (BTSBP, 95%, Aldrich product) was added under stirring at 0 °C. After 30 min of stirring at 0 °C, the mixture was stirred at 40 °C for another 24 h, during which time a white precipitate was formed. The as-synthesized hybrid crystals (denoted as HC, 0.37 g) were recovered by filtration or centrifugation, thoroughly washed with de-ionized H_2O and dried at 60 °C. The yield, based on the hydrolysed BTSBP, was generally 95–100%, suggesting that trace or little P123 was embedded in the crystals obtained. The as-synthesized powders were then heated at 200 °C in air for 30 min to obtain a completely condensed biphenyl–silica hybrid (denoted as HC–H). Carbon–silica hybrid (denoted as HC–C) was obtained by carbonization of the as-synthesized samples in nitrogen or argon at 900 °C for 3 h, during which time the biphenyl groups were converted into carbon.

Fig. 1 shows the field-emission scanning electron microscope (FESEM) images of the as-synthesized HC, which exhibits a uniform micro-sized square-plate morphology. The X-ray diffraction (XRD) pattern (see ESI, Fig. S1†) of the as-synthesized sample (HC) indicates a monoclinic crystal structure with a *C*2(5) space group (a = 6.86, b = 6.94, c = 15.33 Å, β=114.02°, Z = 2), which is similar to the crystal structure of the stable organo bis-silanetriols formed through controlled hydrolysis of the

[a]*Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana 70118, USA. E-mail: ylu@tulane.edu; Fax: (+1) 504 8656744; Tel: (+1) 504 86558272*
[b]*Department of Materials Science and Engineering, The University of Arizona, Tucson, Arizona 85712, USA*
[c]*Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, USA*
[d]*UNM/NSF Center for Micro-Engineered Materials, The University of New Mexico, Albuquerque, New Mexico 87131, USA*
† Electronic supplementary information (ESI) available: XRD, nitrogen adsorption isotherms, ^{29}Si NMR, TGA and TEM images of the hybrids. See DOI: 10.1039/b516985b

Published on 28 February 2006 on http://pubs.rsc.org | doi:10.1039/B516985B
Downloaded by Fudan University on 01 December 2012

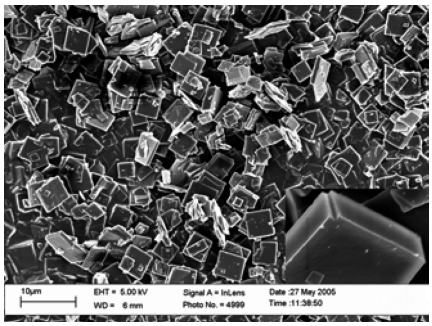

Fig. 1 Representative FESEM images of the as-synthesized hybrid crystals HC. Images taken on a LEO 1530VP microscope operated at 10 kV. Inset: An enlarged view of a crystal.

corresponding bridged precursors in a biphasic medium (*e.g.*, diethyl ether/water).[18,21] The intense diffraction at a 2θ value of 6.3° corresponds to the lamellar ordering along the c-axis, with a *d*-spacing of 1.4 nm that is related to the length of the bridging organic units.[13,18,21] There are no diffraction peaks observed at smaller angles (*e.g.*, less than 5°), indicating the absence of a mesoscopic structure templated by surfactant P123.[22] The as-synthesized hybrid crystals are much less porous, with a very small specific surface area of 6 m^2 g^{-1} (see ESI, Fig. S2†), indicating the close packing of the building molecules.

^{29}Si solid-state nuclear magnetic resonance (NMR) spectroscopy analysis (see ESI, Fig. S3†) indicates that the as-synthesized crystals are composed of uncondensed, completely hydrolysed silsesquioxane, with a single peak at −53.4 ppm.[21] The absence of siloxane bonds (–O–Si–O–) from the condensation reactions of the silanol groups may be attributed to the molecular packing driven by the π–π stacking between the bridging units and the hydrogen-bonding interactions among the silanol groups.[21] Thermogravimetric analysis (TGA) of the as-synthesized crystals HC (see ESI, Fig. S4†) shows that the solid-state polycondensation reaction of the triol groups occurs from 180 °C.[18,21] Therefore, heating the crystals HC at 200 °C promotes silanol condensation, resulting in a lamellar mesostructured organosilica hybrid (HC–H) with an interlamellar distance of ~1.3 nm (see Fig. 2). The condensation reaction among the silanol groups forms cross-linked silica layers alternated by biphenyl organic layers, reducing the interlamellar distance by 0.1 nm. The disappearance of the diffractions in the high angle range indicates the loss of atomic organization inside the silica and biphenyl layers. Nevertheless, the long-range periodicity of the alternating hydrophilic inorganic and hydrophobic organic layers is well retained, while conventional sol–gel processes of similar bridged silsesquioxanes often result in amorphous hybrids.[3,4,8,9]

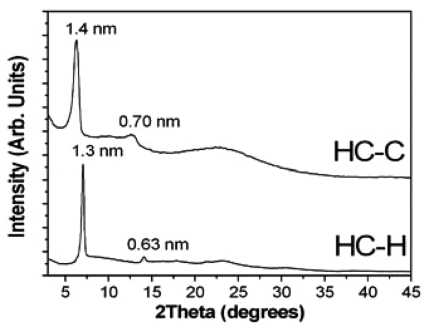

Fig. 2 XRD patterns of the thermally polycondensed hybrid HC–H and the carbonized hybrid HC–C. Patterns recorded on a Siemens D500 diffractometer operating at 40 kV, 30 mA, Cu-K_α radiation, λ = 0.15406 nm.

Conjugated aromatic groups are easily carbonized at high temperatures.[23] Our results here demonstrate that the molecularly ordered lamellar structure remains during the carbonization process of the as-synthesized crystals, forming a carbon–silica layered hybrid. The XRD diffraction pattern of the carbonized hybrid (HC–C) is shown in Fig. 2. The diffractions at 6.3 and 12.6° correspond to a long-range ordered lamellar structure, with an interlamellar distance of 1.4 nm, similar to that of the as-synthesized crystals. In our previous work,[23] the carbonization process destroyed most of the molecular ordering along the pore wall of a mesostructured phenyl–silica hybrid, observed by XRD. In this study, the more stable and dense biphenyl–silica network allows the survival of the molecular ordering. Most interestingly, the carbonization process preserves their morphology very well, as shown in the SEM image (Fig. 3). To our knowledge, this is the first report of a molecularly ordered carbon–silica hybrid with a uniform morphology. The carbonized samples exhibit an increased, but still small surface area of 90 m^2 g^{-1} (see ESI, Fig. S2†) due to the inherent microporosity of synthetic carbon. Solid-state ^{29}Si magic angle spinning nuclear magnetic resonance (MAS-NMR) analysis (see ESI, Fig. S5†) shows that the carbonized material contains 70% quaternary Q_4 Si species ($Si[OSi]_4$) and 30% tertiary T_3 Si species ($CSi[OSi]_3$). Fig. 4 shows the TGA curve of the carbonized particles in oxygen. The weight loss of 51% between 405–575 °C corresponds to the oxidation of

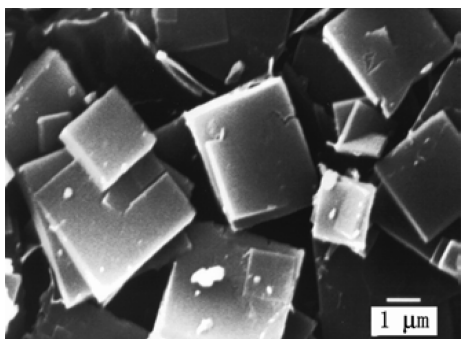

Fig. 3 A representative SEM image of the carbonized hybrid HC–C. Image taken on a JEOL JSM-5410 microscope operated at 20 kV.

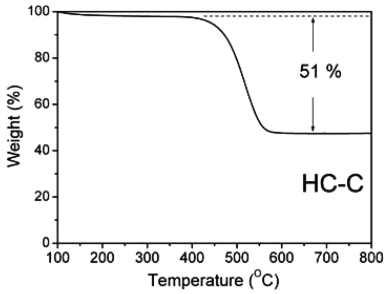

Fig. 4 TGA curve of the carbonized hybrid HC–C in oxygen. TGA performed on a TA Hi-Res TGA 2950 instrument.

This journal is © The Royal Society of Chemistry 2006

Published on 28 February 2006 on http://pubs.rsc.org | doi:10.1039/B516985B
Downloaded by Fudan University on 01 December 2012

carbon in an oxygen atmosphere. The observed value of 51% is close to the calculated carbon content of 56%, indicating the efficient carbonization process. Elemental analysis (see ESI, Fig. S6†) of the carbonized particles by the electron energy-loss spectroscopy (EELS) elemental mapping technique suggests homogeneous distribution of C, Si and O in the materials.

The presence of P123 is very important to obtain uniform crystals due to the phase separation of BTSBP in water without surfactant. Similar to the biphasic medium method,[18,21] the use of THF and H_2O as co-solvents under acidic conditions allows the synthesis of hybrid crystals with the same XRD pattern as that of ESI, Fig. S1.† However, the crystals exhibit random morphology (results not shown). Here, the formation of the as-synthesized HC crystals should involve the hydrolysis of the BTSBP precursor that generates the silanol groups (Si–OH) and the subsequent self-organization of the organo bis-silanetriols in the presence of P123. With the assistance of P123, the hydrophobic BTSBP precursor is well dispersed in water, forming emulsions. Therefore, the hydrolysis and self-assembly processes occur in a confined fashion, *i.e.*, in micelles, resulting in self-assembled crystals with a uniform morphology. Here, collective intermolecular interactions, such as π–π stacking between the bridging units and hydrogen-bonding interactions among the silanol groups, organize the hydrolysed species into crystals.[21] Besides their self-organization, some bridged silsesquioxanes can also co-assemble with Pluronic surfactants during the hydrolysis/polycondensation process, forming a class of periodic mesostructured materials with integral organic functionality.[22] Generally, a co-assembly process involves multiple intermolecular interactions, such as those among the hydrolysed organosilicate species (I), among the surfactant molecules (II), *i.e.*, the driving force to a liquid crystalline phase or micelle, and between organosilicate species and surfactant (III). Balancing the intermolecular interactions is essential to realising a co-assembly process. In this work, predominant interactions (I), *i.e.*, π–π stacking and hydrogen-bonding, favor self-organization of the organosilicate species (*e.g.*, hydrolysed BTSBP) into closely packed crystalline structures (*e.g.*, HC in Fig. 1) rather than co-assembly with P123 through the relatively weak hydrogen-bonding interactions (III). However, weakened interactions (I), by decreasing the bridged groups to phenyl or ethylene, help to balance the intermolecular interactions, allowing their co-assembly with P123 into mesostructured organosilica/surfactant nanocomposites under similar synthesis conditions (results not shown).[22] On the other hand, balanced intermolecular interactions could also be achieved by increasing the interactions (III). For example, ordered mesostructures could be afforded by co-assembling BTSBP with a cationic surfactant (*e.g.*, octadecyltrimethylammonium chloride, OTAC) under basic conditions.[24] The stronger ionic interactions between the organosilicate species and surfactant molecules can balance with the interactions (I) and allow the formation of co-organized biphenyl–silica/OTAC nanocomposites with both mesoscale periodicity and molecular ordering along the pore walls.[24]

In summary, organosilica and carbon–silica hybrids with long-range molecular ordering and uniform particle morphology have been synthesized by thermal polycondensation and carbonization of self-assembled organo bis-silanetriols. The mesoscopic lamellar structure and uniform particle morphology are preserved during the thermal polycondensation and carbonization processes. Due to the complexity of sol–gel reactions leading to hybrids, self- and co-organized pure organo bis-silanetriol molecules with or without surfactant may serve as promising scaffolds to prepare highly organized silica based hybrid nanomaterials with spatially defined structures and functionalities for a broad range of applications.

We thank P. Burnside at Tulane University, Y. Jiang at the University of New Mexico and R. Nieman at Arizona State University for their assistance in XRD, TEM and NMR characterizations, respectively. This work is partially supported by ONR, NSF-CAREER, NSF-NER and DOE PECASE programs

Notes and references

1 R. J. P. Corriu, *Angew. Chem., Int. Ed.*, 2000, **39**, 1376–1398.
2 M. Barboiu, S. Cerneaux, A. van der Lee and G. Vaughan, *J. Am. Chem. Soc.*, 2004, **126**, 3545–3550.
3 R. J. P. Corriu, J. J. E. Moreau, P. Thepot and M. W. C. Man, *Chem. Mater.*, 1992, **4**, 1217–1224.
4 K. J. Shea, D. A. Loy and O. Webster, *J. Am. Chem. Soc.*, 1992, **114**, 6700–6710.
5 D. A. Loy, G. M. Jamison, B. M. Baugher, S. A. Myers, R. A. Assink and K. J. Shea, *Chem. Mater.*, 1996, **8**, 656–663.
6 D. A. Loy, K. Rahimian and M. Samara, *Angew. Chem., Int. Ed.*, 1999, **38**, 555–557.
7 D. W. Schaefer, G. Beaucage, D. A. Loy, K. J. Shea and J. S. Lin, *Chem. Mater.*, 2004, **16**, 1402–1410.
8 F. Ben, B. Boury, R. J. P. Corriu and V. Le Strat, *Chem. Mater.*, 2000, **12**, 3249–3252.
9 B. Boury, F. Ben, R. J. P. Corriu, P. Delord and M. Nobili, *Chem. Mater.*, 2002, **14**, 730–738.
10 B. Boury and R. J. P. Corriu, *Chem. Commun.*, 2002, 795–802.
11 N. G. Liu, K. Yu, B. Smarsly, D. R. Dunphy, Y. B. Jiang and C. J. Brinker, *J. Am. Chem. Soc.*, 2002, **124**, 14540–14541.
12 (*a*) J. J. E. Moreau, L. Vellutini, M. W. C. Man and C. Bied, *J. Am. Chem. Soc.*, 2001, **123**, 1509–1510; (*b*) J. J. E. Moreau, L. Vellutini, M. W. C. Man and C. Bied, *Chem.–Eur. J.*, 2003, **9**, 1594–1599.
13 J. J. E. Moreau, L. Vellutini, M. W. C. Man, C. Bied, J.-L. Bantignies, P. Dieudonné and J.-L. Sauvajol, *J. Am. Chem. Soc.*, 2001, **123**, 7957–7958.
14 J. J. E. Moreau, B. P. Pichon, G. Arrachart, M. W. C. Man and C. Bied, *New J. Chem.*, 2005, **29**, 653–658.
15 J. J. E. Moreau, B. P. Pichon, M. W. C. Man, C. Bied, H. Pritzkow, J.-L. Bantignies, P. Dieudonné and J.-L. Sauvajol, *Angew. Chem., Int. Ed.*, 2004, **43**, 203–206.
16 Y. Luo, J. Lin, H. X. Duan, J. Zhang and C. K. Lin, *Chem. Mater.*, 2005, **17**, 2234–2236.
17 B. Boury, F. Ben and R. J. P. Corriu, *Angew. Chem., Int. Ed.*, 2001, **40**, 2853–2856.
18 G. Cerveau, S. Chappellet and R. J. P. Corriu, *J. Mater. Chem.*, 2003, **13**, 1905–1909.
19 A. Sayari and W. Wang, *J. Am. Chem. Soc.*, 2005, **127**, 12194–12195.
20 K. Okamoto, Y. Goto and S. Inagaki, *J. Mater. Chem.*, 2005, **15**, 4136–4140.
21 (*a*) G. Cerveau, S. Chappellet, R. J. P. Corriu, B. Dabiens and J. Le Bideau, *Organometallics*, 2002, **21**, 1560–1564; (*b*) G. Cerveau, R. J. P. Corriu, B. Dabiens and J. Le Bideau, *Angew. Chem., Int. Ed.*, 2000, **39**, 4533–4537.
22 (*a*) Y. Goto and S. Inagaki, *Chem. Commun.*, 2002, 2410–2411; (*b*) W. H. Wang, S. H. Xie, W. Z. Zhou and A. Sayari, *Chem. Mater.*, 2004, **16**, 1756–1762.
23 J. B. Pang, V. T. John, D. A. Loy, Z. Z. Yang and Y. F. Lu, *Adv. Mater.*, 2005, **17**, 704–707.
24 M. P. Kapoor, Q. H. Yang and S. Inagaki, *J. Am. Chem. Soc.*, 2002, **124**, 15176–15177.