Soft Matter

COMMUNICATION

Biomimetic morphogenesis of micropottery: helical coiling of mesostructured silica nanofibers†

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Biomimetic morphogenesis of sophisticated mesostructured silica micropottery with a novel 3D hierarchically ordered structure and diverse morphologies was realized by hydrolyzing tetraethylsiloxane (TEOS) in concentrated HNO_3 solutions containing cetyltrimethylammonium bromide (CTAB). It was proposed that the unique micropottery was self-organized by helical coiling of hexagonally ordered mesostructured silica nanofibers with the assistance of the NO_3^- counterion, which is amazingly reminiscent of the manufacture of pottery vessels by wheel shaping in ancient Oriental Asia. The observed self-organization of the mesostructured silica micropottery may open new avenues towards the microfabrication of advanced materials with hierarchical 3D architectures.

The high degree of sophistication and miniaturization found in natural materials has long been a source of fascination and inspiration.[1] Life is able to make unique, exquisite biominerals with hierarchical organization and complex form;[2] in particular, diatoms create porous silica frustules exhibiting an incredible variety of sophisticated shapes and multifunctional properties, which have afforded rich inspiration for the development of nanotechnology and advanced materials.[3] Till now, significant efforts have been devoted to unraveling the morphogenesis mechanisms in biomineralization and synthesizing advanced materials with tunable morphologies and patterns biomimetically.[4–8] In this regard, self-organization and transformation of anisotropic nano-objects under non-equilibrium conditions, such as buckling, folding, twisting, and coiling of deformable filaments and thin films, have shown great promise in delicate morphogenesis as well as three-dimensional (3D) microfabrication.[9,10]

Among the limited success achieved in the morphogenesis of inorganic materials with complex form in the lab, the morphological control of surfactant-templated mesoporous silica is remarkable.[4,11] For the ordered mesoporous silica obtained in surfactant-rich systems, a wide variety of shapes such as gyroids, spheres,

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polyhedrons, and various one-dimensional (1D) structures (*e.g.*, fibers, ribbons, and tubes) have been obtained.[11,12] However, a generally accepted comprehensive understanding of morphogenesis of the shaped mesostructures is still lacking. While topological defects were initially proposed to explain the morphogenesis of curve-shaped mesostructured silica based on folding and deformation of a pre-ordered structure, a coiling mechanism was adopted as a general approach to the assembly of circular mesostructures with a structural hierarchy.[13] Recently, helical mesostructured silica has attracted considerable interest since it represents a new fashion for the design and application of chiral materials.[14] It is noteworthy that there are numerous reports on the synthesis of helical mesostructured silica nanofibers using achiral surfactants as the template although the exact mechanism for the origin of the helical mesostructure from achiral amphiphiles is still debatable.[15] Despite the remarkable progress in the morphology-controlled synthesis of mesostructured silica, it remains a great challenge to realize the self-organization of complex mesostructured silica with hierarchical 3D architectures.

Recently, we reported a controllable synthesis of helical mesoporous silica nanofibers *via* a seeding-growth method in a quaternary system consisting of cetyltrimethylammonium bromide (CTAB), tetraethylsiloxane (TEOS), HNO_3 and water, and an entropy-driven mechanism was proposed to explain their formation.[16] Herein, one-pot synthesis of micrometre-sized, 3D hierarchically ordered silica mesostructures with intricate pottery-like morphologies was realized in this system with a high concentration of HNO_3. A helical coiling mechanism was proposed for the self-organization of the sophisticated mesostructured silica micropottery, which is amazingly reminiscent of the manufacture of pottery vessels by wheel shaping in ancient Oriental Asia.[17] To the best of our knowledge, this is the first synthesis of 3D hierarchically structured micropottery made of mesoporous silica, which may open new avenues towards the microfabrication of advanced materials with hierarchical 3D architectures.

The synthesis of mesostructured silica micropottery was achieved simply by hydrolyzing TEOS in a concentrated HNO_3 solution containing CTAB at room temperature. In a typical synthesis, 2.5 mL of aqueous CTAB solution (10 mM) was mixed with 2.5 mL of HNO_3 solution (3.5 M), which was followed by the addition of 0.2 mL of TEOS under vigorous stirring, giving a CTAB concentration of 5 mM and a HNO_3 concentration of 1.75 M. Then, the reaction solution was thermostatted at 23 °C for 12 h under static conditions. The solid product was collected, washed with water, and dried at 60 °C overnight. Calcination was carried out in air at 550 °C

for 6 h when necessary. The synthesis was also conducted at different HNO_3 concentrations and in the presence of other acids with different anions (e.g., HBr and HCl) under otherwise similar conditions. The obtained products were characterized by scanning electronic microscopy (SEM, Hitachi S4800, 2 kV), transmission electronic microscopy (TEM, JEOL JEM 200CX, 160 kV), high-resolution TEM (HRTEM, Hitachi H9000, 100 kV), powder X-ray diffraction (XRD, Rigaku Dmax-2000, Cu Kα), and nitrogen adsorption–desorption measurements (Micromeritics ASAP 2010) with the pore size distribution calculated from the adsorption curve using the Brunauer–Joyner–Halenda (BJH) method.

As shown in Fig. 1, sophisticated micropottery vessels exhibiting a rich variety of morphologies and surface patterns were obtained. The overview image shown in Fig. 1a suggests the large-scale production of the micrometre-sized hollow vessels with a pottery-like morphology. The pottery vessels usually consist of a gyroidal base (typically 1–5 μm in diameter) and a hollow circular column standing on the base. The zoom-in images of individual vessels (Fig. 1b–i) clearly show their diverse, exquisite appearance, like jar, crock, vase, cooking vessel, or even artwork pottery. Notably, some vessels exhibit obvious circular wrinkles and buckling patterns on the surface of the hollow columns. The high-magnification side view (Fig. 1j and k) and top view (Fig. 1l and m) of individual open mouths suggest that there are uniform, parallel channels (~100 nm or less in diameter) aligned circumferentially along the hollow vessel wall, and most of the uppermost circular rims are not completely smooth with the existence of a single breakpoint, indicating that the hollow part of the vessels may form by helical coiling of nanofibers. It is worth mentioning that similar micropottery vessels with diverse, exquisite appearance can be readily obtained from repeated experiments although it is not possible to obtain two vessels with exactly the same patterns and architectures.

The mesostructure of the obtained micropottery was characterized by the XRD and nitrogen sorption measurements. As shown in Fig. 2a, the XRD pattern of the as-obtained micropottery vessels clearly reveals a well-ordered two-dimensional (2D) hexagonal mesostructure with a lattice constant of ~4.0 nm, typical for the cationic surfactant-templated mesostructured silica obtained in acidic solutions.[18] Our preliminary experimental results showed that after calcination at 550 °C for template removal, the XRD pattern did not show considerable changes and the micropottery vessels essentially preserved their original morphologies. The nitrogen sorption isotherms of the calcined micropottery vessels show a steep capillary condensation in the relative pressure (p/p_0) range of 0.2–0.35, indicating uniform mesopores with a BJH pore size of ~2.6 nm (Fig. 2b). The BET surface area and mesopore volume were measured to be 1295 m^2 g^{-1} and 0.96 cm^3 g^{-1}, respectively. These results suggest that the obtained pottery vessels were made of mesostructured silica with a hexagonal structure, indicating the formation of mesostructured silica micropottery with a 3D hierarchically ordered structure, i.e., a hexagonal mesostructure and a helical coiling structure at the nanometre scale and a 3D ordered pottery-like morphology at the micrometre scale.

The hierarchical structure of the mesostructured silica micropottery was further characterized by TEM and HRTEM observations, which are shown in Fig. 3. It can be seen that the parallel nanofibers aligned circumferentially along the hollow vessel wall are evident (Fig. 3a and b). The TEM image presented in Fig. 3c shows an abrupt breakpoint of the coiling nanofiber ~100 nm in diameter, and the HRTEM image shown in Fig. 3d clearly shows the presence of hexagonally close packed channels with a periodic spacing of ~3.7 nm inside the nanofibers. Fig. 3e shows the TEM image of a relatively small pottery vessel. The HRTEM images taken from two different areas exhibit clear lattice fringes attributed to hexagonally closed packed channels (Fig. 3f and g), confirming that the whole vessel is made of hexagonally ordered mesostructured silica with their channels parallel to the coiling nanofibers. These results confirmed the formation of mesostructured silica micropottery with a 3D hierarchically ordered structure. Furthermore, some mesostructured silica micropottery vessels with nanofibers extruding from the vessel
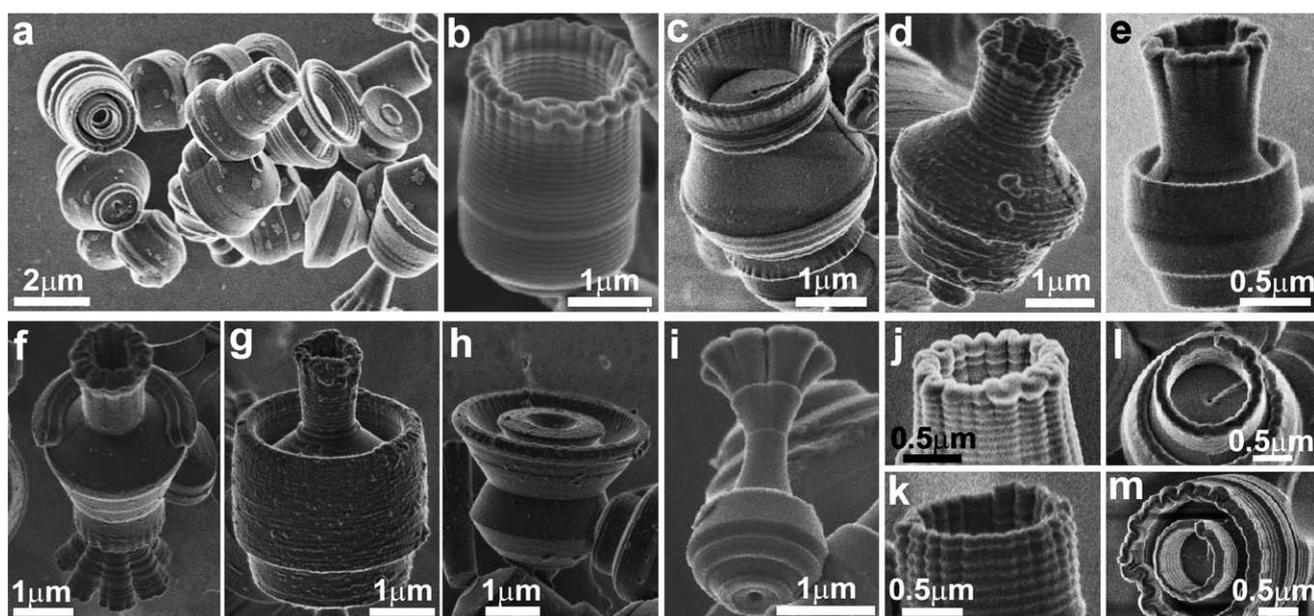

Fig. 1 SEM images of mesostructured silica micropottery vessels.
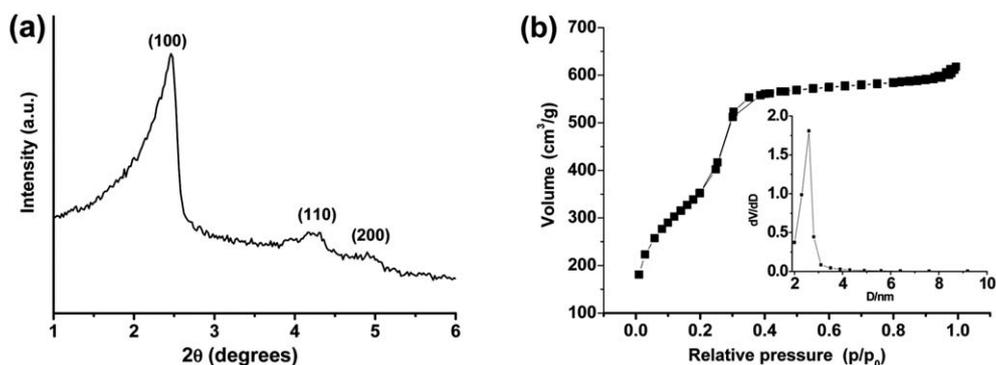
Fig. 2 (a) XRD pattern of mesostructured silica micropottery vessels. (b) Nitrogen adsorption–desorption isotherms and the pore size distribution (inset) of the calcined micropottery vessels.
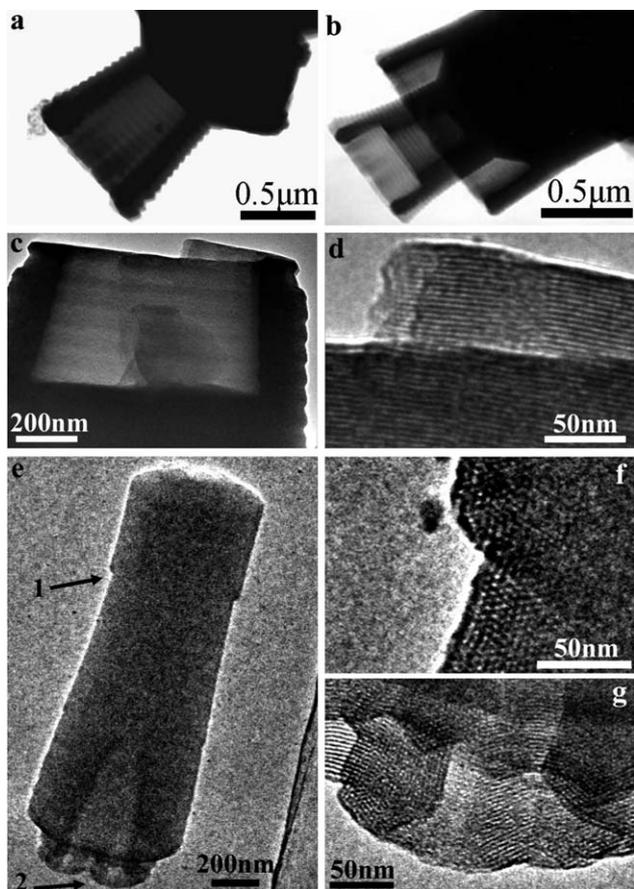

Fig. 3 TEM (a–c and e) and HRTEM (d, f and g) images of mesostructured silica micropottery vessels. Plate (d) is an amplified image of Plate (c). Plates (f) and (g) are amplified images of the areas 1 and 2 in Plate (e), respectively.

rim were harvested, as shown in Fig. 4, which strongly indicates that the self-organization of the 3D hierarchically ordered micropottery vessels from helical coiling of mesostructured silica nanofibers.

The growth process of the mesostructured silica micropottery was investigated by examining the products obtained at the early stages of their formation (Fig. S1, ESI†). Only gyroids were obtained instead of hollow vessels after a reaction time of 20 min. A number of micropottery vessels with hollow circular columns grown on the flat

surface of gyroids were obtained when the reaction time was prolonged to 3 h. The micropottery vessels would be the dominant morphology if the reaction was further increased to 12 h, as shown in Fig. 1. Based on these observations, a helical coiling mechanism is tentatively proposed for the formation of the novel mesostructured silica micropottery, which is schematically illustrated in Scheme 1a. The fast hydrolysis and condensation of TEOS in a concentrated HNO_3 solution containing CTAB resulted in the immediate formation of circular mesostructured gyroids by the proposed coiling mechanism.[13] Then, the abrupt decrease in the concentration of reacting species occurred owing to the quick formation of a lot of gyroidal seeds, which would lead to the formation of mesostructured nanofibers as well as their helical coiling into hollow vessels on the flat surface of the gyroidal seeds under non-equilibrium conditions.[9] Meanwhile, many buckling patterns would form through self-assembly of the curved compliant vessel wall.[10] Finally, sophisticated mesostructured silica micropottery vessels exhibiting a breakpoint existing on the vessel rim with diverse morphologies were obtained. Amazingly, this helical coiling mechanism is reminiscent of the manufacture of pottery vessels by wheel shaping in Oriental Asia
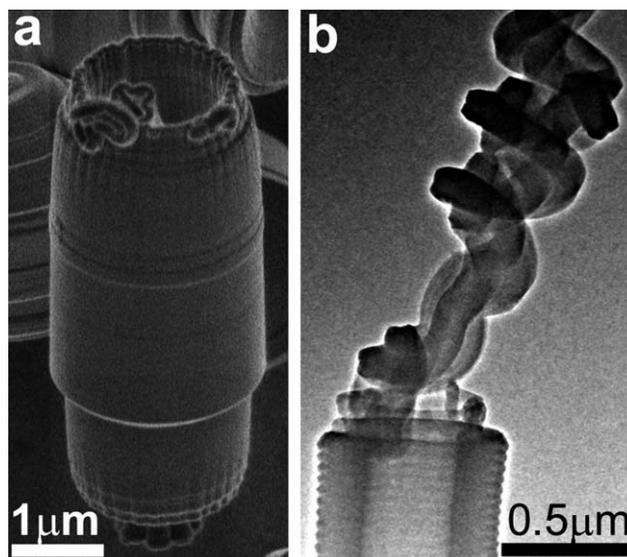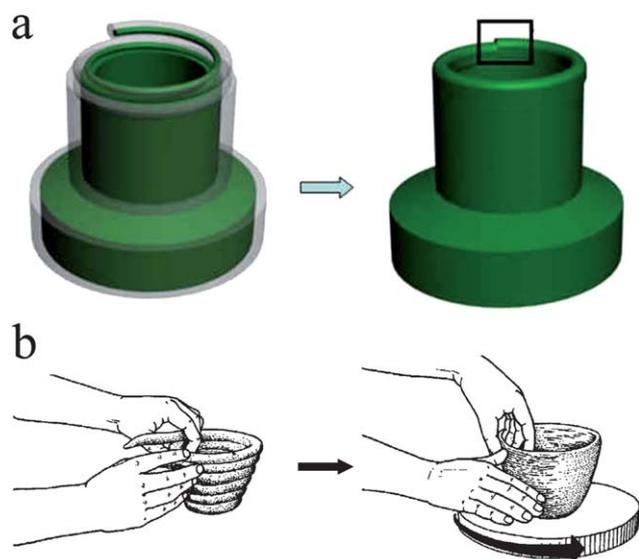

Fig. 4 SEM (a) and TEM (b) images of mesostructured silica micropottery vessels with nanofibers extruding from the vessel rim.

Scheme 1 (a) Schematic illustration of spontaneous coiling of mesostructured silica nanofibers into micropottery vessels. The boxed area indicates the presence of a breakpoint on the vessel rim. (b) Manufacture of pottery vessels by wheel shaping in Oriental Asia during the 4th to 3rd millennium BC. Reprinted with permission from ref. 17, copyright 1998 Academic Press.

during the 4th to 3rd millennium BC.[17] Moreover, this helical coiling mechanism might offer some implications on the biomineralization of spiral seashells with a helical structure.

It was found that a highly concentrated HNO₃ solution was crucial for the formation of the mesostructured silica micropottery. When HNO₃ was replaced with HBr, a large amount of curve-shaped particles together with a few micropottery vessels were obtained under otherwise similar conditions; when HCl was used instead, only gyroids were obtained without the appearance of any pottery vessels (Fig. S2, ESI†). In addition, the concentration of the HNO₃ solution had a significant effect on the morphology of the obtained mesostructured silica (Fig. S3, ESI†). If the HNO₃ concentration was kept above 1.75 M but less than 2 M (Caution! HNO₃ is highly oxidative), the overall morphologies of the silica products were essentially unchanged. When the HNO₃ concentration was decreased from 1.75 M to 0.7 M, gyroids became the predominant product. Only gyroids were produced at a HNO₃ concentration of 0.35 M. If the HNO₃ concentration was further decreased to 0.175 M, a large amount of mesostructured silica nanofibers coexisted with a minority of silica gyroids.

It has been documented that in acidic media, there exists a bridge counterion (X^-) at the interface of positively charged silica oligomers (I^+) and cationic surfactants (S^+), and the relatively weak $S^+X^-I^+$ interaction favors topological construction of diverse morphologies.[18] The strength of the binding of the counterion X^- to surfactant micelles follows the Hofmeister sequence: $NO_3^- > Br^- > Cl^- > SO_4^{2-}$, with nitrate being the highest binding strength.[11] Consequently, HNO₃ tends to form very long micelles with CTAB and is a suitable acid source for preparing silica fibers with parallel nanochannels; moreover, HNO₃ favors a fast condensation reaction of cationic silicate species at the micelle surface.[11] In the current synthesis of mesostructured silica micropottery, a faster reaction rate and a larger tendency to form mesostructured nanofibers are favorable

for the growth and helical coiling of mesostructured silica nanofibers. As for the effect of the HNO₃ concentration, it might be rationalized by considering that a high enough HNO₃ solution is required to bring about a quick formation of a lot of gyroidal seeds, leading to an abrupt decrease in the concentration of reacting species and hence subsequent growth and coiling of nanofibers under non-equilibrium conditions. Nevertheless, an exact formation mechanism remains to be elucidated.

In conclusion, exquisite mesostructured silica micropottery with a novel 3D hierarchically ordered structure and diverse morphologies was successfully produced by biomimetic morphogenesis in concentrated HNO₃ solutions. It was proposed that the self-organization of the unique micropottery resulted from helical coiling of hexagonally ordered mesostructured silica nanofibers assisted by the NO_3^- counterion. Amazingly, this mechanism is reminiscent of the manufacture of pottery vessels by wheel shaping in ancient Oriental Asia. The observed self-organization of the mesostructured silica micropottery might shed some light on the biomineralization of spiral biominerals and open new avenues towards the micro-fabrication of hierarchical 3D architectures with advanced functions.

Acknowledgements

Notes and references

1 C. Sanchez, H. Arribart and M. M. G. Guille, *Nat. Mater.*, 2005, **4**, 277.
2 F. C. Meldrum and H. Cölfen, *Chem. Rev.*, 2008, **108**, 4332.
3 (*a*) D. Losic, J. G. Mitchell and N. H. Voelcker, *Adv. Mater.*, 2009, **21**, 2947; (*b*) N. Nassif and J. Livage, *Chem. Soc. Rev.*, 2011, **40**, 849.
4 H. Yang, N. Coombs and G. A. Ozin, *Nature*, 1997, **386**, 692.
5 J. M. García-Ruiz, E. Melero-García and S. T. Hyde, *Science*, 2009, **323**, 362.
6 (*a*) J. Aizenberg, D. A. Muller, J. L. Grazul and D. R. Hamann, *Science*, 2003, **299**, 1205; (*b*) C. Li and L. Qi, *Angew. Chem., Int. Ed.*, 2008, **47**, 2388.
7 (*a*) H. Cölfen and S. Mann, *Angew. Chem., Int. Ed.*, 2003, **42**, 2350; (*b*) A.-W. Xu, Y. Ma and H. Cölfen, *J. Mater. Chem.*, 2007, **17**, 415; (*c*) R.-Q. Song and H. Cölfen, *CrystEngComm*, 2011, **13**, 1249.
8 (*a*) H. Imai, *Top. Curr. Chem.*, 2007, **270**, 43; (*b*) L. Qi, *Coord. Chem. Rev.*, 2010, **254**, 1054.
9 S. Mann, *Nat. Mater.*, 2009, **8**, 781.
10 X. Chen and J. Yin, *Soft Matter*, 2010, **6**, 5667.
11 H.-P. Lin and C.-Y. Mou, *Acc. Chem. Res.*, 2002, **35**, 927.
12 (*a*) Y. Wan and D. Zhao, *Chem. Rev.*, 2007, **107**, 2821; (*b*) Z. Yang, Y. Lu and Z. Yang, *Chem. Commun.*, 2009, 2270.
13 F. Marlow, A. S. G. Khalil and M. Stempniewicz, *J. Mater. Chem.*, 2007, **17**, 2168.
14 H. Qiu and S. Che, *Chem. Soc. Rev.*, 2011, **40**, 1259.
15 (*a*) B. Wang, C. Chi, W. Shan, Y. Zhang, N. Ren, W. Yang and Y. Tang, *Angew. Chem., Int. Ed.*, 2006, **45**, 2088; (*b*) S. Yang, L. Zhao, C. Yu, X. Zhou, J. Tang, P. Yuan, D. Chen and D. Zhao, *J. Am. Chem. Soc.*, 2006, **128**, 10460; (*c*) J. Wang, W. Wang, P. Sun, Z. Yuan, B. Li, Q. Jin, D. Ding and T. Chen, *J. Mater. Chem.*, 2006, **16**, 4117; (*d*) Y. Han, L. Zhao and J. Y. Ying, *Adv. Mater.*, 2007, **19**, 2454; (*e*) P. Yuan, L. Zhao, N. Liu, G. Wei, Y. Wang, G. J. Auchterlonie, J. Drennan, G. Q. Lu, J. Zou and C. Yu, *Chem.–Eur. J.*, 2010, **16**, 1629; (*f*) J. Ye, H. Zhang, R. Yang, X. Li and L. Qi, *Small*, 2010, **6**, 296.
16 L. Zhou, G. Hong, L. Qi and Y. Lu, *Langmuir*, 2009, **25**, 6040.
17 V. Roux, *J. Archaeol. Sci.*, 1998, **25**, 747.
18 H.-P. Lin, C.-P. Kao, C.-Y. Mou and S.-B. Liu, *J. Phys. Chem. B*, 2000, **104**, 7885.