



Metal-Organic Frameworks Reactivate Deceased Diatoms to be Efficient CO₂ Absorbents

Dingxin Liu, Jiajun Gu,* Qinglei Liu, Yongwen Tan, Zhuo Li, Wang Zhang, Yishi Su, Wuxia Li, Ajuan Cui, Changzhi Gu, and Di Zhang*

Living diatoms, one of the most common types of phytoplankton, consume 20% of global CO₂ and yield 40% of marine primary productivity through photosynthesis.^[1] This active process stops with their deaths and the remains (cell walls, or frustules) deposit onto the sea/lake floor, forming diatomite. Here we report that these silica frustules, which were previously regarded as inert with respect to CO2 absorption, can be activated and converted to highly efficient CO₂ absorbents by forming composites with some metal-organic frameworks (MOFs). For example, the diatomite composite composed of ca. 57.2 wt% zeolitic imidazolate framework 8 (ZIF-8) - ZIF-8/diatomite (Z8/D) - shows CO2 storage capacity of 0.80 mmol g^{-1} at 298 K, 1 bar, which is ca. 20% greater than that of pure ZIF-8. Detailed analyses show that the additional CO₂ taken up by MOF/D is stored in the micro-/mesopores of frustules, which are inaccessible without the help of MOFs. This work demonstrates the combination of an inert CO₂ absorbent with an active one, producing a novel material that doubles the CO2 uptake efficiency per gram of ZIF-8 and MOF-5. Most importantly, the pronounced ability of diatomite to store CO2 (4.3 wt%, at 298 K and 1 bar, even higher than that of pure ZIF-8 and MOF-5) has implications for understanding the functionality of frustules, the starting point for the carbon fixation process performed by diatoms that has an impact on retarding global warming.

The concentration of CO_2 in water (ca. 10 μ M) is far lower^[1,2] than in the atmosphere (ca. 387 µM). Instead, the main form of carbon in aqueous environments is bicarbonate (HCO₃⁻, ca. 1990 $\mu M).^{[1,\bar{2}]}$ Living diatoms, which are famous for their biosilica cell walls (frustules) with hierarchical porous structures,[3-10] have thus developed an effective CO₂ concentration mechanism (CCM) to transport the environmental carbon into their chloroplasts for photosynthesis.^[1,2] Although this mechanism is poorly understood at present,^[1,2] it is generally believed that carbonic anhydrases (CAs), a group of enzymes catalyzing

Dr. D. X. Liu, Prof. J.-J. Gu, Prof. Q. L. Liu, Dr. Y. W. Tan, Z. Li, Dr. W. Zhang, Dr. Y. S. Su, Prof. D. Zhang State Key Laboratory of Metal Matrix Composites Shanghai Jiao Tong University 800 Dongchuan Road, Shanghai, 200240, P. R. China E-mail: gujiajun@sjtu.edu.cn; zhangdi@sjtu.edu.cn Prof. W. X. Li, Dr. A. J. Cui, Prof. C. Z. Gu Beijing National Laboratory of Condensed Matter Physics Institute of Physics Chinese Academy of Sciences 8 Zhongguancun South 3 Street, Beijing, 100190, P. R. China

DOI: 10.1002/adma.201304284

the reversible reaction between CO₂ and HCO₃⁻, play an important role in controlling carbon transport pathways.^[1,2,11-14] For example, to help the carbon source penetrate the cell membrane of a diatom, extracellular CA (eCA), which is located on the diatom frustules and in the periplasmic space, transforms the negatively charged HCO₃⁻ in water to CO₂. The resulting CO₂ subsequently diffuses through membranes into the cell for photosynthesis.^[1,2] Such a natural CCM or CO₂ capture process ceases after the deaths of diatoms. Their frustule sediments form diatomite on sea/lake floors, with ca. 1 billion metric tons being deposited since the Cretaceous Period (66-138 million vears ago).^[15]

Nevertheless, CO_2 locally generated by CA from $HCO_3^$ may escape from the diatom cells into the water.^[12-14] Living diatoms have thus generated some intracellular organelles to store CO2.[1] In comparison, extracellular CCM processes (eCA induced) are made more difficult by large through holes (ca. 20 nm-1 μ m)^[4-10] in frustules, the unique cell walls made of biosilica, in contrast to other semipermeable walls in plants. These through holes make it difficult for eCA to maintain the difference in CO₂ pressure between the periplasmic space and the environment. It is thus reasonable to suppose that, like the walls of bundle-sheath cells,^[12] which store CO₂ in C₄ plants, the frustules of diatoms might serve as buffers to maintain CO₂ concentration in cells with the help of eCA.

However, although diatomite has been used as an absorbent for liquid ever since it was first applied by Alfred Nobel to stabilize nitroglycerin in fabricating dynamite in the 1860s, no evidence has been reported that these deposited frustules can be used as absorbents for CO₂ gas.^[15,16] We notice that one of the major differences between the lifeless diatomite and living diatoms is the existence of CA that can locally accumulate CO₂ molecules.^[2,12] Just as a mat on a wet floor can keep moisture beneath it, enhancing CO2 concentration in the vicinity of frustules by means of CA can promote CO₂ adsorption. We thus take an analogous approach, assembling MOF layers as "CA mats" on the surfaces of lifeless diatom frustules. The synthesis route adopted here comprises three steps: 1) a surface amination process of diatom frustules full of hydroxyls, 2) coordination of Zn^{2+} on the surface of frustules, and 3) MOF formation^[17] via hydrothermal synthesis. Technical details can be found in Scheme S1 in the Supporting Information. ZIF-8,^[17-20] a prototypical MOF^[21-26] that is famous for its chemical and thermal stability and can accumulate CO2 either in its molecular cage or in interspatial areas,^[27] is first applied here (Figure 1a). Figure 1b-h and Figure S1 in the Supporting Information confirm the successful fabrication of Z8/D. The ZIF-8 nanoparticles (ca. 30 nm in size, calculated from X-ray diffraction data in Figure S1b using the Debye-Scherer





www.MaterialsViews.com



Figure 1. Characterization of as-synthesized Z8/D. a) Route to MOFs/D. MOFs serve as "mats" on the surfaces of "wet (CO₂) floors (diatomite)". b) Scanning electron microscopy (SEM) image of a diatom frustule covered by ZIF-8. Elemental mapping results are shown in the right column, with the elements of ZIF-8 denoted by the red frame. Zn was used to assess the amount of ZIF-8. Strong carbon signals originated from the carbon tape for the SEM observation. c,d) Close-up views of (b). ZIF-8 crystallites covered the surfaces of the frustules uniformly. e) High-resolution transmission electron microscopy (TEM) image of ZIF-8 crystallites. f) Selected area diffraction pattern of Z8/D. Inset: The diffraction pattern from commercial ZIF-8 (Z1200). g) ¹³C CP/MAS NMR spectra of powders of Z8/D, Z8/D ground in liquid N₂ for 40 min, and Z1200 (top to bottom; Larmor frequency: 75.47 MHz; MAS frequency: 10 kHz). These results confirm that there were no significant byproducts in the as-synthesized samples. h) Micro-Raman spectra of Z8/D and Z1200. The inset indicates the position where the data were recorded. The peak at 879 cm⁻¹ (1067 cm⁻¹) denotes the (anti)symmetric stretching mode of Si-O-Si. The remaining peaks are from ZIF-8.^[17] Scale bars: b) 2 μm; c) 500 nm; d) 100 nm; e) 5 nm; h) 20 μm.

formula) covered the surfaces of the frustules uniformly. Note that we also ground the Z8/D samples in liquid N₂ for up to 40 min to identify the guest chemicals possibly left in diatomite structures, but no significant byproducts could be detected in the ¹³C cross-polarization (CP)/magic-angle spinning (MAS) NMR spectrum either (Figure 1g). To determine the weight ratio between SiO₂ and ZIF-8 in Z8/D, we measured the amount of Zn present using an inductively coupled plasma optical emission spectrometer (ICP-OES), as the original diatomite did not contain significant amounts of this element. The weight ratio of SiO₂ to ZIF-8 was about 42.8:57.2 (Table S1 in the Supporting Information), which will be used

later to evaluate the contribution of the ZIF-8 in Z8/D to $\rm CO_2$ capture capacity.

Interesting results were achieved when we studied the ability of Z8/D to store CO₂. As shown in **Figure 2**a, at 298 K, the average gravimetric CO₂ adsorption capacity of Z8/D powders from five different batches of samples was ca. 0.80 mmol g⁻¹ under 1 bar, 20% higher than that of commercial ZIF-8 (Basolite Z1200, BASF).^[27–29] In comparison, the average amount of CO₂ taken up by diatomite can be ignored. Note that diatomite in this control group were treated in the same way as Z8/D except that step 2 was skipped. Considering that the ZIF-8 content of Z8/D was just 57.2 ± 4.4 wt%, the Z8/D powders exhibited a

www.advmat.de



www.MaterialsViews.com



Figure 2. Gas uptake properties of MOFs/silica. a) CO_2 uptake isotherms on Z8/D at 298 K. Note that (1) the amount of CO_2 taken up by diatomite can be considered negligible; (2) Z8/D takes up more CO_2 than pure ZIF-8 does, even when only ca. 57.2 wt% as much ZIF-8 is present; (3) the Z8/D isotherms show hysteresis loops not found in pure ZIF-8. b) CO_2 uptake isotherms on Z8/D ground in liquid N₂ for various times. Inset: The particle size change during the grinding process. c) Gas uptake properties of MOFs/silica at various temperatures under 1 atm. Maximum gas uptake (left columns), additional gas uptake via combination (middle columns), and additional gas uptake in solid-state volume per gram of silica (right columns) for Z8/D, M5/D, and Z8/SBA-15 are presented. If diatomite is used as the silica substrates instead of SBA-15 (shaded area), the bonus gas adsorption is in the range of 17.5–27.8 mm³ per gram of diatomite, revealing the CO_2 capture ability of frustules.

20% increase in CO₂ uptake with only half the amount of ZIF-8 by weight. Such a coupling effect was not observed in N₂ and Ar isotherms on Z8/D (Figure S2, Supporting Information). Moreover, the CO₂ adsorption/desorption curve of Z8/D was not reversible, showing a hysteresis loop that did not present in CO₂ isotherms on ZIF-8.^[18]

Since the amination process adopted to fabricate Z8/D (Scheme S1, Supporting Information) might increase the CO₂ uptake itself,^[30,31] we conducted several experiments to differentiate a structural effect from such a chemical effect. Figure 2b shows CO₂ isotherms for a series of Z8/D powders ground in liquid N₂ in an agate mortar for 10–40 min. The maximum CO₂ uptake amount drastically decreased to 0.37 mmol g⁻¹ (56.06% of pure ZIF-8) under 1 bar for Z8/D powders ground for 40 min. The loss of enhancement (or "bonus") in CO₂ uptake by the combination of ZIF-8 and diatomite indicated that this effect was structure-originated rather than amination-originated, since the Zn present and functional groups of Z8/D did not apparently change during the grinding process (Table S2

and Figure S3, Supporting Information). Such a result is consistent with the observed low CO_2 uptake on the diatomite that had been subjected to amination treatment (Figure 2a), the NMR spectra of Z8/D, and the gas adsorption on various MOF/ silica systems to be presented later in this Communication.

We then chose C_2H_2 ,^[32–34] an adsorbate similar to CO_2 in kinetic diameter (3.3 Å), polarization, and sublimation temperature (-84 °C vs. -76 °C), as a probe to confirm whether such a coupling phenomenon happens only with CO_2 or with other gases as well (Figure S4, Supporting Information). Although the additional uptake amount of C_2H_2 as a result of combination was different from that of CO_2 (middle columns in Figure 2c), the solid-state volumes of the additionally absorbed CO_2 and C_2H_2 were consistent in value (right columns in Figure 2c). We further replaced the ZIF-8 by MOF-5 (M5),^[35,36] another prototype MOF, and replaced diatomite by SBA-15,^[37] a commercial silica product with mesopores, to generate M5/D (Table S3 and Figure S5, Supporting Information) and Z8/SBA-15 (Table S4 and Figure S6, Supporting Information), respectively. Results





Figure 3. Cross-sectional analyses of frustules. a) SEM image of the cross section of the epitheca of a centric diatom. Inset: TEM image of the selected area. Black lines (stronger electron adsorption) can be identified. b–e) High-magnification TEM images of the selected areas in (a) show alternately stacked porous layers. f) Mechanisms for frustules to trap CO_2 . g) CO_2 uptake isotherms on raw diatomite at 298 K. Under 20 atm (ca. 196 m underwater), up to 1.32 wt% CO_2 can be stored in lifeless frustules even without the help of CA. Scale bars: a) 1 μ m (inset: 100 nm); b,c) 20 nm; d,e) 10 nm.

(Figure S5–S7, Table S5–S7, Supporting Information) show that when diatomite was used as a substrate to form composites with MOFs, the additional gas storage amount in solid-state volume arising from combination was maintained (ca. 17.50–27.80 mm³ per gram of diatomite, right columns in Figure 2c). However, when diatomite was replaced by SBA-15, the additional CO₂ uptake drastically decreased (equivalent to ca. 5.90 mm³ in solid-state volume per gram of silica, probably from the amination process). These results acquired from different silica substrates (diatomite and SBA-15), various MOFs (MOF-5 and ZIF-8), and different adsorbates (CO₂ and C₂H₂) strongly indicate that the extra gases absorbed by MOFs/D exist in the solid state in those pores provided by diatom frustules.

To understand how these frustule sediments can store CO_2 gas, we cut them open using focused-ion-beam (FIB)



www.MaterialsViews.com

machining (Figure 3a) to study their inner structures with TEM. Surprisingly, we found that the frustules are composed of alternately packed dense/loose nanolayers (inset of Figure 3a) rather than the randomly distributed pores reported by Vrieling et al.^[38] Under higher resolutions (Figure 3b-e), mesopores (ca. 2-8 nm in diameter) in loose layers and micropores (≤2 nm in diameter) in dense layers can be identified. We also observed such structures in the frustules of fresh diatoms without any chemical treatments (Figure S8, Supporting Information). Similar architectures can be found in petroleum geology, where loose layers serve as oil reservoirs and dense layers as seals. It is understandable that, under lower pressures (e.g., 1 atm), these dense lavers can prevent enormous CO₂ adsorption (Figure 2a), otherwise CO₂ will soon saturate the frustules and be difficult to release, as the planktonic diatoms living in the photic zone practically bear higher water pressures.^[39] But once gas molecules succeed in squeezing into frustules (Figure 3f), dense layers will act as throttle valves to trap adsorbates in the loose layers. This assumption has been supported by CO₂ uptake experiments conducted under higher pressures, where the lifeless frustules themselves can store CO₂ up to ca. 1.32 wt% under 20 atm, or equivalently at 196 m beneath the water surface (the photic zone depth in the open ocean, Figure 3g).

Although quantitative analyses of this buffering process are still under way, present experimental evidence can provide a new insight into the CCM in living diatoms (Scheme 1). To our understanding, the CCM arising from the frustule of a living diatom is usually neglected,^[1,11-14] probably because there are holes through the frustules ranging in diameter from 20 nm to 1 μ m,^[4–10] which causes a balance of dissolved ions and gases at the two sides of the wall. But these holes

might also cause CO_2 leakage as mentioned above (Scheme 1a). In this way, the CO_2 buffering ability of frustules, or a "physical Hatch–Slack pathway",^[12] may help diatoms maintain their intracellular CO_2 concentrations (Scheme 1b) to avoid surfeiting of or starving for CO_2 .

To our knowledge, this is the first demonstration that diatom frustules can act as CO_2 buffers, an important link in a successive biological CCM chain. The strategy described here also has the potential to convert millions of tons of diatomite to active CO_2 absorbent. Further combinations of different MOFs and other biological structures (such as $CaCO_3$ cell walls of coccolithophorids^[40]) might render this group of new materials suitable for a broad range of applications, including gas storage and gas separation. Moreover, since detailed kinetic models have not yet been constructed in this Communication,

MATERIALS

www.advmat.de

Materials

www.MaterialsViews.com



Scheme 1. Functionality of diatom frustules. a) Present understanding.^[1,2,11–13] Unlike normal semipermeable cell walls, the frustules of diatoms have through holes (ca. 20 nm to ca. 1 μ m in diameter) that allow CO₂ leakage (see the broken line). b) Hypothesis proposed here. Frustules serve as CO₂ buffers and prevent the CO₂ from escaping.

experimental and theoretical analyses that can quantitatively clarify this CO_2 concentration process are required in the future.

Experimental Section

Materials: Fresh diatoms (*Coscinodiscus sp.*, Figure S8 in the Supporting Information) were provided by the Institute of Oceanology, Chinese Academy of Sciences, Qingdao, China. Diatomite (ca. 60% *Coscinodiscus sp.*, ca. 30% *Cyclotella sp.*, and ca. 5% *Melosira sp.*) were purchased from Celite Co., Ltd., China. To fabricate MOFs/D, diatomite (ca. 0.6 g) was first pretreated with HCl solution (37%) for 5 h, rinsed in deionized water, and dried in air. Then we used ethylenediamine (purchased from Sinopharm Chemical Reagent Co., Ltd., P. R. China, ≥99.0%) to activate the diatomite (Scheme S1, Supporting Information). The surface-activated diatomite was then soaked in water saturated with Zn(NO₃)₂:4H₂O (2.61 g or 1 × 10⁻² mol, from Merck, Darmstadt, Germany, ≥98.5%) for 5 h, rinsed in deionized water, and air-dried. ZIF-8 and MOF-5 were generated on the surface of the Zn²⁺ coordinated silica by means of hydrothermal synthesis.^[17,35]

Characterization: SEM analyses were conducted on an FEI Quanta 250 SEM (20 kV) equipped with an energy dispersive spectrometer (EDS) (Oxford Instruments, 80 mm² detector). Samples were treated by Au sputtering before observation. HRTEM analyses were carried out using an FEI Tecnai-F20 (200 kV) and a JOEL 2010F (200 kV) instrument. ¹³C CP/MAS NMR spectroscopy analyses were conducted on a Bruker Avance III 300 NMR spectrometer. The spectra were measured at a Larmor frequency of 75.47 MHz, a MAS frequency of 10 kHz, and a sample temperature of 293 K. Micro-Raman spectra were recorded using a Renishaw inVia micro-Raman instrument (50x short focal length objective). A 785 nm output from an argon-ion laser was used as the light source.

Gas Uptake: CO₂ uptake (Table S8, S12, and S13, Supporting Information) was measured using an IGA 002 gravimetric analyzer (Hiden Isochema, UK). N₂, Ar, and C₂H₂ isotherms (Table S9–S11, Supporting Information) were recorded on an ASAP 2020 accelerated surface area and porosimetry system (volumetric adsorption analyzer, Micromeritics, Norcross, GA, USA).

FIB Machining: FIB processing was conducted on an FEI Helios NanoLab 600i DualBeam system. 30 kV Ga ions with beam current of 80 pA and 7 pA, and 2 kV Ga ions with a beam current of 5 pA were successively used to cut the frustules (ca. 80 nm in thickness).

Full methods are available in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51271116 and 51171110), the National Basic Research Program of China (973 Program, Grant No. 2012CB619600), and the Shanghai Science and Technology Committee (Grant No. 10JC1407600). The authors thank Prof. Huihua Zhou and the Beijing National Center for Electron Microscopy, Tsinghua University, China, for the TEM observations.

> Received: August 26, 2013 Published online: November 27, 2013

- B. M. Hopkinson, C. L. Dupont, A. E. Allen, F. M. M. Morel, Proc. Natl. Acad. Sci. USA 2011, 108, 3830–3837.
- [2] A. J. Milligan, F. M. M. Morel, Science 2002, 297, 1848-1850.
- [3] D. L. Rabosky, U. Sorhannus, Nature 2009, 457, 183-186.
- [4] J. Toster, K. S. Iyer, R. Burtovyy, S. S. O. Burgess, I. A. Luzinov, C. L. Raston, J. Am. Chem. Soc. 2009, 131, 8356–8357.
- [5] D. Losic, J. G. Mitchell, N. H. Voelcker, Adv. Mater. 2009, 21, 2947–2958.
- [6] Z. H. Bao, E. M. Ernst, S. Yoo, K. H. Sandhage, Adv. Mater. 2009, 21, 474–478.
- [7] F. C. Meldrum, H. Colfen, Chem. Rev. 2008, 108, 4332-4432.
- [8] Z. H. Bao, M. R. Weatherspoon, S. Shian, Y. Cai, P. D. Graham, S. M. Allan, G. Ahmad, M. B. Dickerson, B. C. Church, Z. T. Kang, H. W. Abernathy, C. J. Summers, M. L. Liu, K. H. Sandhage, *Nature* 2007, 446, 172–175.
- [9] E. K. Payne, N. L. Rosi, C. Xue, C. A. Mirkin, Angew. Chem. Int. Ed. 2005, 44, 5064–5067.
- [10] M. Sumper, E. Brunner, Adv. Funct. Mater. 2006, 16, 17-26.
- [11] Y. Xu, L. Feng, P. D. Jeffrey, Y. G. Shi, F. M. M. Morel, Nature 2008, 452, 56–61.
- [12] J. V. Moroney, A. Somanchi, Plant Physiol. 1999, 119, 9-16.
- [13] E. Granum, J. A. Raven, R. C. Leegood, Can. J. Bot. 2005, 83, 898–908.
- [14] K. Roberts, E. Granum, R. C. Leegood, J. A. Raven, Photosynth. Res. 2007, 93, 79–88.
- [15] R. D. Crangle Jr., in *Minerals Yearbook (2011)*, U.S. Geological Survey (USGS), Washington, DC 2012.
- [16] Y. S. Bae, R. Q. Snurr, Angew. Chem. Int. Ed. 2011, 50, 11586-11596.
- [17] K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. D. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* 2006, 103, 10186–10191.
- [18] G. Lu, J. T. Hupp, J. Am. Chem. Soc. 2010, 132, 7832-7833.
- [19] S. R. Venna, M. A. Carreon, J. Am. Chem. Soc. 2010, 132, 76– 78.
- [20] D. Fairen-Jimenez, S. A. Moggach, M. T. Wharmby, P. A. Wright, S. Parsons, T. Duren, J. Am. Chem. Soc. 2011, 133, 8900–8902.
- [21] N. Stock, S. Biswas, Chem. Rev. 2012, 112, 933-969.
- [22] K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae, J. R. Long, *Chem. Rev.* 2012, *112*, 724–781.
- [23] J. R. Li, J. Sculley, H. C. Zhou, Chem. Rev. 2012, 112, 869–932.
- [24] J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown, J. Liu, J. Chem. Soc. Rev. 2012, 41, 2308–2322.
- [25] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* **2008**, *319*, 939–943.

ADVANCED MATERIALS



- [26] D. Britt, H. Furukawa, B. Wang, T. G. Glover, O. M. Yaghi, Proc. Natl. Acad. Sci. USA 2009, 106, 20637–20640.
- [27] J. Perez-Pellitero, H. Amrouche, F. R. Siperstein, G. Pirngruber, C. Nieto-Draghi, G. Chaplais, A. Simon-Masseron, D. Bazer-Bachi, D. Peralta, N. Bats, *Chem. Eur. J.* **2010**, *16*, 1560–1571.
- [28] C. Zhang, R. P. Lively, K. Zhang, J. R. Johnson, O. Karvan, W. J. Koros, J. Phys. Chem. Lett. 2012, 3, 2130-2134.
- [29] H. Amrouche, S. Aguado, J. Perez-Pellitero, C. Chizallet, F. Siperstein, D. Farrusseng, N. Bats, C. Nieto-Draghi, J. Phys. Chem. C 2011, 115, 16425–16432.
- [30] R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi, T. K. Woo, *Science* **2010**, *330*, 650–653.
- [31] A. Demessence, D. M. D'Alessandro, M. L. Foo, J. R. Long, J. Am. Chem. Soc. 2009, 131, 8784–8786.
- [32] J. R. Li, R. J. Kuppler, H. C. Zhou, Chem. Soc. Rev. 2009, 38, 1477–1504.
- [33] R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, *Nature* 2005, 436, 238–241.

- [34] S. C. Xiang, W. Zhou, J. M. Gallegos, Y. Liu, B. L. Chen, J. Am. Chem. Soc. 2009, 131, 12415–12419.
- [35] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, Nature 1999, 402, 276–279.
- [36] H. X. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gandara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'Keeffe, O. Terasaki, J. F. Stoddart, O. M. Yaghi, *Science* **2012**, *336*, 1018–1023.
- [37] D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548–552.
- [38] E. G. Vrieling, T. P. M. Beelen, R. A. van Santen, W. W. C. Gieskes, Angew. Chem. Int. Ed. 2002, 41, 1543–1546.
- [39] M. A. Tiffany, in *The Diatom World* (Eds.: J. Seckbach, J. P. Kociolek), Springer, New York **2011**, p. 201.
- [40] M. D. Iglesias-Rodriguez, P. R. Halloran, R. E. M. Rickaby, I. R. Hall, E. Colmenero-Hidalgo, J. R. Gittins, D. R. H. Green, T. Tyrrell, S. J. Gibbs, P. von Dassow, E. Rehm, E. V. Armbrust, K. P. Boessenkool, *Science* 2008, *320*, 336–340.