Dangling Bond Dynamics on the Silicon (100)-2×1 Surface: Dissociation, Diffusion, and Recombination

Marcus McEllistrem, Matthew Allgeier, John J. Boland*

The dynamics of dangling bond (DB) diffusion was studied after deuterium desorption from the silicon (100)-2×1 surface. At elevated temperatures, paired DB sites produced after desorption unpaired as deuterium atoms hopped from adjacent dimers. Below 620 kelvin, the unpaired configuration most commonly observed corresponded to two DBs on adjacent silicon dimers. At higher temperatures, unpaired DBs executed one-dimensional walks along the dimer rows, and recombination was observed with the same partner after walks lasting many minutes. The frequency and extent of these excursions increased with temperature. Above 660 kelvin, complete dissociation was observed and was sometimes followed by recombination by means of partner exchange. The implications for low-temperature materials growth are discussed.

Hydrogen desorption is an essential step in the growth of materials by chemical vapor deposition (CVD). Desorption regenerates surface DBs to provide reactive sites for further growth (*1*). However, the presence of DBs is a necessary but insufficient condition for growth; dissociative chemisorption of CVD gas-phase precursors requires at least two DBs at nearby surface sites (*2*). Under typical growth conditions, H atoms present on the surface are mobile, so that the spatial distribution of DBs can differ dramatically from the paired configuration produced by desorption. This mobility is an important consideration for low-temperature materials growth, because desorption is slow compared to surface diffusion. In principle, a small DB population may adopt a configuration that is not conducive to further growth. The probability of such configurations is not known and requires an understanding of the dynamics of DBs.

We describe an elevated-temperature scanning tunneling microscopy (STM) study of the dissociation, diffusion, and recombination of DBs produced after D_2 thermal desorption from the Si(100)-2×1:D surface. Paired DBs unpaired by D atom hopping from an adjacent dimer. An unpaired configuration involving DBs on adjacent dimers was frequently observed, and the number of these sites increased steadily with sample temperature T_s. Pairs of DBs also dissociated and underwent one-dimensional (1D) walks along the dimer rows of the Si(100) surface. Remarkably, for low DB populations, these sites eventually recombined after walks lasting upwards of 10 min.

We used an Omicron VT-STM (*3*) to study a single Si(100) sample, which was cleaned by repeated flashing to 1400 K. The Si(100)-2×1:D monodeuteride surface was prepared by a 600-K saturation exposure of the clean Si(100)-2×1 surface to atomic D (*4*). Direct-current heating was used, and T_s was measured post-facto by a chromel-alumel thermocouple epoxied to the front of the sample and was reproducible to within 20 K. The sample bias was typically ±1.6 V, and low tunneling currents (200 pA or less) were used; the sample bias was calibrated by nulling the zero-point current crossing observed in STM current-voltage measurements.

The tunneling conditions were chosen so as to minimize interactions between the surface and probe tip, and in particular to avoid the possibility of tip-induced D_2 desorption or D-atom diffusion by means of either of two documented mechanisms: vibrational heating or electronic excitation (*5*). Electronic excitation was excluded on the basis of our observation that the threshold for D_2 desorption was greater than 5 V, even for $T_s > 600$ K. Similarly, vibrational heating was not significant because tunneling currents of 60 pA (that is, currents 1% of that needed to desorb D_2) produced D-atom dynamics that were indistinguishable from those observed under the optimal imaging conditions reported herein. Moreover, the probability for desorption by vibrational heating decreases nearly 300-fold as T_s is increased from 11 to 300 K (*6*), so that tip-induced vibrational heating is negligible at 600 K and above.

To prepare a controlled population of DBs, we heated the Si(100)-2×1:D surface to 710 K for several minutes. We then reduced T_s until DB diffusion was not evident on a time scale of many minutes to hours. By gradually increasing T_s, conditions were established where at most one or two hopping events occurred between successive frames. The STM images were then recorded in a continuous scanning mode with a minimum frame time of about 15 s for an area of 10 nm by 10 nm (about 350 dimers). A filled-state topograph of the DB population recorded at 635 K (Fig. 1A) reveals stable bright sites centered along the Si(100) dimer rows. These sites are paired DBs located on a single dimer and are the immediate products of D_2 desorption (*7*). In an empty-state topograph (Fig. 1B), these sites have a pronounced node, consistent with the weak π character of paired DBs on the Si(100)-2×1 surface (*7*).

Occasionally a paired DB site transformed into a site that was fuzzy in appearance (Fig. 1, B and C). Although clearly fluxional, the feature shown is positioned on a single dimer row but shifted along the row compared to the location of the original DB site. Paired DB sites and fuzzy sites were both brighter than the surrounding D-covered surface, but fuzzy sites appeared brightest under low bias, indicating a larger density of states at the Fermi energy (*7*). Transformations of this kind were frequently observed at elevated temperatures. However, under conditions where surface diffusion was limited (600 to 620 K), fuzzy sites often remained stable for many minutes. The transformation in Fig. 1 shows that fuzzy and paired DB sites are intimately related: both are confined to a single dimer

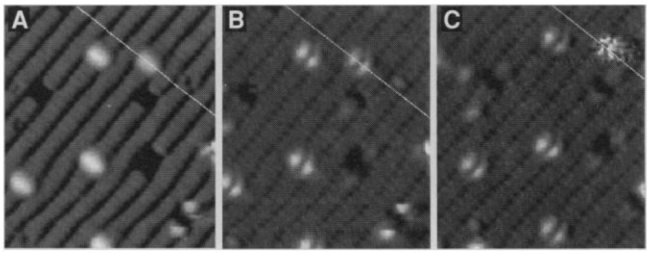

Fig. 1. A series of STM topographs of the Si(100)-2×1:D surface after 450 s of D_2 desorption at 710 K. (**A**) Filled-state image and (**B**) empty-state image, acquired on forward and backward scans, respectively. (**C**) Empty-state image acquired 80 s after (A) and (B). The site on the white line converts from stable to fluxional; it later converted back to a stable site (not shown). Imaging conditions: T_s = 635 K; acquisition rate, 40 s per frame; image area, 8.7 nm by 7.6 nm, tunneling current I_t = 200 pA; sample voltage V_{samp} = −1.8 V in (A) and V_{samp} = +2.12 V in (B) and (C).

Venable and Kenan Laboratories, Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290, USA.

*To whom correspondence should be addressed.

row and are comprised of two DBs, although the configuration is different for each.

After we increased T_s to 670 K, the number of paired DB sites decreased, whereas the number of fluxional sites increased (Fig. 2A). Under these conditions, fluxional sites often appeared as elongated features that extended over many dimer units but were still confined to a single dimer row. The distribution and spatial extent of these fuzzy sites constantly changed on the surface. The extended feature noted in Fig. 2A was significantly contracted 100 s later (Fig. 2B), whereas others became more extended. Evidently, there was significant long-range motion on the surface at this temperature, the details of which will be described elsewhere (8).

The structure of these fluxional sites can be probed by carefully choosing T_s and the data acquisition conditions. We recorded a 10-min series of STM images at 620 K (Fig. 3). A paired DB site changes into a fluxional site that is similar in appearance to the previously discussed feature in Fig. 1. The fluxional site then dissociates into two smaller fluxional features, which hop up and down along the dimer row, recombine to form a large fluxional site, and convert back to a paired DB site at a new dimer location. These images, together with many others, lead us to conclude that the small, mobile fluxional features are Si dimers that contain a single D atom and an unpaired DB (9) (Fig. 4). The large composite fluxional sites (Fig. 1C and Fig. 3, B and E), then, are single D atoms on each of two adjacent dimers; from this point forward, we will refer to these sites as predissociated DB pairs. Two possible configurations for these sites are shown in Fig. 4, row B. These assignments are consistent with the fact that unpaired DBs exhibit empty and filled states close to the Fermi energy and explain why these sites are brighter than paired DB sites, which have a small gap at this energy (7). Their fluxional character results from D-atom hopping between sites on the same dimer. Under the present conditions, the tip does not induce intradimer or interdimer hopping, as confirmed by the absence of preferential motion while scanning along or perpendicular to the dimer row direction and by the fact that interdimer hopping was completely suppressed for $T_s \leq \sim 565 \pm 20$ K and intradimer hopping was suppressed for $T_s < 500$ K.

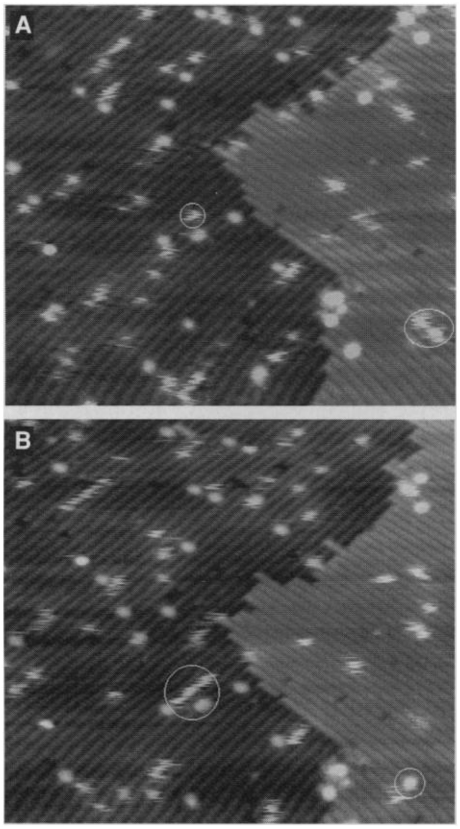

Fig. 2. (**A**) Filled-state topograph of the Si(100)-2×1:D surface after 240 s of D_2 desorption at 710 K. (**B**) Topograph acquired 100 s after (A). The majority of DBs have diffused a distance of several dimers between (A) and (B), of which two sites are highlighted. The two fluxional sites at the lower right in (A) recombine to form a paired DB site in (B), whereas the central small fluxional site in (A) becomes elongated in (B). Imaging conditions: T_s = 670 K; acquisition rate, 100 s per frame; image area, 44 nm by 49 nm; I_t = 200 pA; V_{samp} = −1.66 V.

These data show that even though the paired DB configuration has the lowest energy, as a result of a weakly stabilizing π interaction (*10, 11*), the population of unpaired DBs becomes more pronounced at higher temperatures. The driving force behind this phenomenon is the increased configurational entropy of two unpaired DB sites compared with that of a single paired DB site. The number of accessible configurations increases with temperature as unpaired DBs execute 1D walks that sample additional neighboring sites. This process is also reversible: As the temperature is decreased, the excursion length for unpaired DBs becomes reduced. At low temperatures, DB excursions are limited to nearest neighbor sites, but become more frequent and pronounced at higher temperatures. However, because hopping rates also increase at higher temperatures, these 1D walks are recorded as bright, elongated fuzzy features that extend and contract along the Si dimer rows (Fig. 2).

Analysis of these data also provide information on the types of events that occur on the surface. In contrast to previous results reported for Cl atoms on Si(100) that showed intradimer hopping at room temperature, all DB motion in the present study was suppressed below 500 K. Although intradimer hopping was more facile than interdimer hopping in both studies, in the Cl

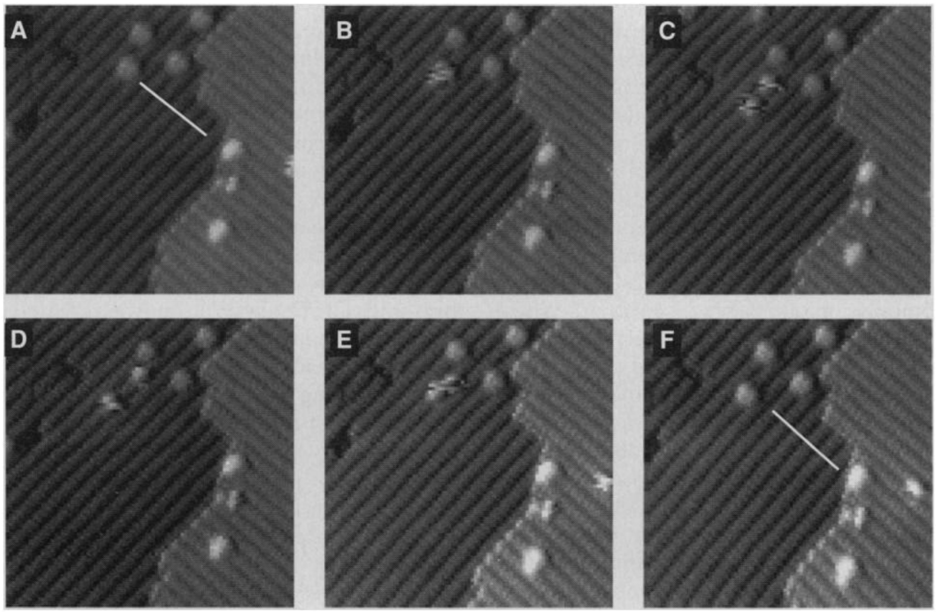

Fig. 3. Selected filled-state topographs from a series of STM images of the Si(100)-2×1:D surface after 120 s of D_2 desorption at 710 K. (**A**) A pair of DBs, connected by a white bar. (**B**) The paired DBs convert to a predissociated site. (**C**) The fluxional site dissociates into two smaller fluxional features. (**D**) These two features hop up and down along the dimer row. (**E**) They eventually recombine to form a large fluxional site. (**F**) Finally, the site converts back into a pair of DBs at a new dimer location. The paired DBs in (F) are two dimers away from their original position in (A). Imaging conditions: T_s = 620 K; acquisition rate, 50 s per frame; image area, 25 nm by 25 nm; I_t = 200 pA; V_{samp} = −1.66 V. Total time between (A) and (F) is 550 s.

case intradimer atom motion was influenced by the STM tip and was facilitated by the presence of a bridge-bonded configuration (12) (in which a Cl atom is centered over a Si dimer), a bonding geometry not available for D atoms. In agreement with theoretical (13) and experimental (14) studies, hopping is essentially confined along the dimer row direction, but limited hopping events between rows have been observed. There is no evidence for long hops encompassing more than a single dimer site. In instances where such hops were recorded between consecutive images, the hopping rates were such that sequential events were statistically probable. Under the present conditions, only unpaired DB sites were observed to hop. However, at high temperatures, dissociation and recombination occur rapidly, resulting in the apparent concerted motion of paired DB sites. This motion is demonstrated by the shifting positions of paired DB sites (for example, the paired DB site on the line) in the image sequence in Fig. 5. Apparent motion of paired DBs is also observed at location Z (following DB recombination in Fig 5A). At location X, a paired DB site dissociates and subsequently recombines, whereas at Y, an unpaired DB collides with a paired DB site, resulting in DB exchange. At location W, two unpaired DBs recombine across a missing-dimer defect and subsequently traverse the defect. Although DB motion across defects is frequently observed, DBs rarely diffuse away from defects; dimers at the edge of missing-dimer defects apparently serve as preferred sites for DBs.

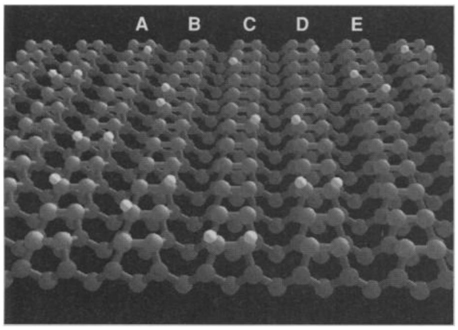

Fig. 4. Ball-and-stick model of the Si(100)-2×1:D surface. The DBs are shown as white spheres, but D atoms (one D atom for every surface Si atom not bearing a DB) have been omitted for clarity. Paired DBs are shown in rows A, C, and D; unpaired DBs are shown in the same rows. Two possible DB configurations are indicated for the predissociated DB configuration in row B. Unpaired DBs interacting across a dimer row are shown for DBs that are positioned directly opposite (rows C and D) and staggered (rows D and E).

The apparent concerted motion of paired DB sites shown in Fig. 5 suggests that there is an attractive interaction between individual DBs. This behavior is not unexpected, because it is well established that DBs on the same dimer are stabilized by a weak π interaction (10, 11). This type of interaction, however, may also stabilize DBs in other configurations. Recent calculations (10) and STM studies involving halogen dissociation (15) indicate the presence of a stabilizing interaction between unpaired DBs on adjacent dimers that are located on the same side of the dimer row. This DB configuration also stabilizes C defects on clean Si(100)-2×1 and is identical to the predissociated DB configuration (16) (Fig. 4, row B). Although the DB separation in this case is larger than that for DBs on the same dimer (0.38 versus 0.23 nm), the overlap is significant because the DBs are parallel and not directed away from each other (17).

Other, even more separated DB configurations also appear to be stable. In the first of a series of four images recorded at T_s = 620 K (Fig. 6A), two unpaired DBs are identified that are located on adjacent dimer rows. One of these DBs appears to be pinned, presumably because of the presence of a missing-dimer defect in the adjacent row. The second DB, although free to move, is significantly less mobile than other isolated DBs shown in this series (Fig. 6). Presumably, this DB is stabilized by an interaction across the dimer row with the first DB. These two DBs appear to maintain a staggered configuration throughout. In other images, DBs on neighboring rows remote from the influence of defects align on adjacent dimers and remain immobile for many minutes. Long-range interactions of this type are probably the result of either through-space DB interactions or lattice strain. The latter may result from strain introduced by the presence of buckled dimers with unpaired DBs on a surface that consists predominantly of symmetric dimers. The free-electron density associated with the symmetric dimer structure of the monohydride

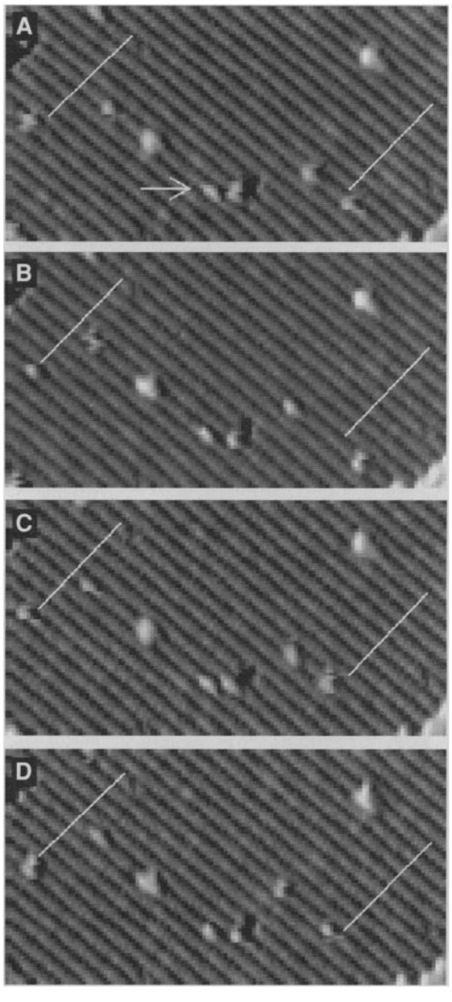

Fig. 6. Four images from a series of filled-state STM topographs of the Si(100)-2×1:D surface that span a 7-min period. Unpaired DBs diffuse along dimer rows, but the indicated DBs interacting across a dimer row [indicated with an arrow in (A)] show significantly reduced motion. Imaging conditions: T_s = 620 K; acquisition rate, 52 s per frame; image area, 11 nm by 22 nm; I_t = 200 pA; V_{samp} = +1.40 V.

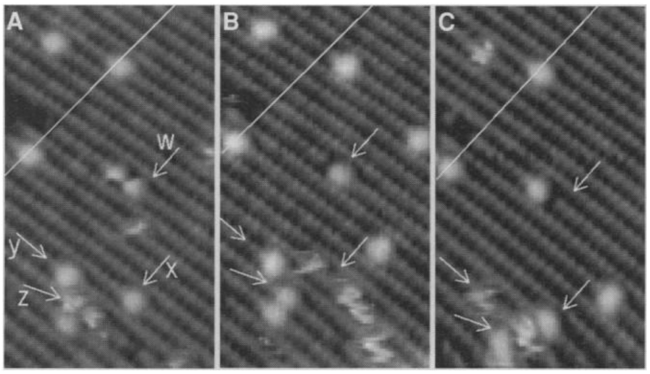

Fig. 5. Selected filled-state topographs of the Si(100)-2×1:D surface. Images are of the same surface shown in Fig. 2. Most DBs in this sequence undergo change: one paired DB site [on the line in (**A**)] appears to hop two dimers away in (**B**) and then return in (**C**); a second paired DB site at lower right in (B) appears to have moved one dimer in (C). Sites W and Z show DB recombination; site X shows dissociation in (B) and recombination in (C); paired DB site at Y becomes fluxional in (C) after interacting with an unpaired DB. Imaging conditions: T_s = 670 K; acquisition rate, 30 s per frame; image area, 17 nm by 7.6 nm; I_t = 200 pA; V_{samp} = −1.66 V.

surface is low (*7*), so that strain fields introduced by unpaired DBs may not be effectively screened.

The DB diffusional dynamics reported here has important implications for surface processes and, in particular, materials growth. It demonstrates that at low temperatures, because of an attractive interaction, a majority of DB sites are likely to be paired and hence available for dissociative chemisorption and further growth. Had it been otherwise, growth would necessarily become a trimolecular process involving two uncorrelated surface DBs and an incident precursor molecule. At higher temperatures, entropy drives DBs to unpair, and DB diffusion becomes increasingly random. However, the number of DB sites is correspondingly larger (because of desorption), so that a statistically significant fraction of sites is present in a configuration that favors growth. Although the present study involves the Si(100) surface, these same arguments may well apply to a variety of systems, particularly if through-space DB interactions prove to be the origin of these local correlations.

REFERENCES AND NOTES

1. J. M. Jasinski, B. S. Meyerson, B. A. Scott, *Annu. Rev. Phys. Chem.* **38**, 109 (1987).
2. Y. Suda, D. Lubben, T. Mooka, J. E. Greene, *J. Vac. Sci. Technol. A* **8**, 61 (1990); S. M. Gates, *Surf. Sci.* **195**, 307 (1988).
3. Omicron Vakuumphysik, Taunsstein, Germany.
4. J. J. Boland, *Adv. Phys.* **42**, 129 (1993).
5. T.-C. Shen *et al.*, *Science* **268**, 1590 (1995).
6. E. T. Foley *et al.*, *Phys. Rev. Lett.*, in press.
7. J. J. Boland, *ibid.* **67**, 1593 (1991).
8. M. McEllistrem and J. J. Boland, in preparation.
9. These data differ from previous STM studies of DBs on the Si(100)-2×1:H surface after H_2 desorption (*7*). Specifically, DBs were previously found to largely be paired, whereas the present study shows DBs that unpair and can be frozen in unpaired configurations once T_s is too low for D atoms to diffuse. The different behaviors can be explained by the different thermal treatments used. In the present study, T_s was increased slowly, D_2 was desorbed over a period of several minutes, and the sample was then cooled to the imaging temperature. In the previous study, by contrast, H_2 was desorbed in a rapid anneal-and-quench thermal cycle, and the surface was imaged at room temperature. The rapid method minimizes the time available for the DBs to unpair, resulting in a population of predominantly paired DBs.
10. A. Vittadini, A. Selloni, M. Casarin, *Phys. Rev. B* **49**, 11191 (1994).
11. P. Nachtigall, K. D. Jordan, K. C. Janda, *J. Chem. Phys.* **95**, 8652 (1991); M. P. D. D'Evelyn, Y. L. Yang, L. F. Sutcu, *ibid.* **98**, 3560 (1993); U. Hofer, L. Li, T. F. Heinz, *Phys. Rev. B* **45**, 9485 (1992).
12. G. A. deWijs and A. Selloni, *Phys. Rev. Lett.* **77**, 881 (1996).
13. C. J. Wu and E. A. Carter, *Phys. Rev. B* **46**, 4651 (1992).
14. J. H. G. Owen, D. R. Bowler, C. M. Goringe, K. Miki, G. A. D. Briggs, *ibid.* **54**, 14153 (1996).
15. In an earlier halogen study [J. J. Boland, *Science* **262**, 1703 (1993)], we noted that at room temperature, two Cl atoms that were bonded on neighboring dimers showed a distinct preference to be on the same side of the dimer row. This preference remained even under imaging conditions where single Cl atoms (and unpaired DBs) readily hopped back and forth between sites on the same dimer.
16. A preliminary analysis of hopping rates to determine the relative energies of paired and unpaired configurations indicated that the predissociated configuration is stabilized compared with that of unpaired DBs, although not to the extent of paired DBs.
17. R. J. Hamers and U. K. Koehler, *J. Vac. Sci. Technol. A* **7**, 2854 (1989).
18. We thank E. J. Buehler and M. Fouchier for programming assistance, and M. Rubinstein and J. L. Whitten for insightful discussions. Financial support by NSF under contracts DMR 9509790 and DMR 9413999 is gratefully acknowledged.

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Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores

Dongyuan Zhao, Jianglin Feng, Qisheng Huo,
Nicholas Melosh, Glenn H. Fredrickson, Bradley F. Chmelka,*
Galen D. Stucky*

Use of amphiphilic triblock copolymers to direct the organization of polymerizing silica species has resulted in the preparation of well-ordered hexagonal mesoporous silica structures (SBA-15) with uniform pore sizes up to approximately 300 angstroms. The SBA-15 materials are synthesized in acidic media to produce highly ordered, two-dimensional hexagonal (space group *p6mm*) silica-block copolymer mesophases. Calcination at 500°C gives porous structures with unusually large interlattice *d* spacings of 74.5 to 320 angstroms between the (100) planes, pore sizes from 46 to 300 angstroms, pore volume fractions up to 0.85, and silica wall thicknesses of 31 to 64 angstroms. SBA-15 can be readily prepared over a wide range of uniform pore sizes and pore wall thicknesses at low temperature (35° to 80°C), using a variety of poly(alkylene oxide) triblock copolymers and by the addition of cosolvent organic molecules. The block copolymer species can be recovered for reuse by solvent extraction with ethanol or removed by heating at 140°C for 3 hours, in both cases, yielding a product that is thermally stable in boiling water.

Large pore–size molecular sieves are much in demand for reactions or separations involving large molecules (*1*, *2*). Since mesoporous molecular sieves such as hexagonally ordered MCM-41 were discovered by Mobil Corporation scientists in 1992 (*3*, *4*), surfactant-templated synthetic procedures have been extended to include a wide range of compositions, and a variety of conditions have been developed for exploiting the structure-directing functions of electrostatic, hydrogen-bonding, and van der Waals interactions associated with amphiphilic molecules (*5*–*16*). Typically, these materials are synthesized under conditions where silica-surfactant self-assembly (*16*) occurs simultaneously with condensation of the inorganic species, yielding mesoscopically ordered composites. For example, MCM-41 materials prepared with cationic cetyltrimethylammonium (CTA$^+$) surfactants commonly have *d*(100) spacings of about 40 Å, which after calcination yield a hexagonally ordered porous solid with uniform pore sizes of 20 to 30 Å (*5*–*9*, *12*). Cosolvent organic molecules, such as 1,3,5-trimethylbenzene (TMB) used to expand the pore size of MCM-41 up to 100 Å (*3*, *4*), unfortunately yield materials with less-resolved x-ray diffraction (XRD) patterns, particularly near the high end of this size range, for which a single broad diffraction peak is often observed (*9*). Extended thermal treatment during synthesis gives expanded pore sizes up to ~50 Å (*17*). We have used postsynthesis treatment, by subsequently heating the product obtained from an alkaline S^+I^- synthesis at room temperature in distilled water at pH = 7, to obtain pore sizes as large as ~60 Å (*9*) without the need for organic swelling agents. Using CTA$^+$ surfactant species in an L_3 sponge phase, McGrath *et al.* (*18*) created siliceous solids with large, uniform, but disordered pore assemblies. Pinnavaia and co-workers (*11*) used nonionic surfactants in neutral aqueous media to synthesize worm-like disordered mesoporous silica with uniform pore sizes of 20 to 58 Å. To increase the dimensions of pore structures produced in such inorganic-organic com-

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D. Zhao, Q. Huo, G. D. Stucky, Department of Chemistry and Materials Research Laboratory, University of California, Santa Barbara, CA 93106, USA.
J. Feng, Department of Chemistry and Center for Quantized Electronic Structures, University of California, Santa Barbara, CA 93106, USA.
N. Melosh, G. H. Fredrickson, B. F. Chmelka, Materials Research Laboratory and Department of Chemical Engineering, University of California, Santa Barbara, CA 93106, USA.

*To whom correspondence should be addressed. E-mail: bradc@engineering.ucsb.edu (B.F.C.); stucky@chem.ucsb.edu (G.D.S.)