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16. When the effect of spin-orbit coupling is taken into account, the classical barrier height on the ground adiabatic Cl + H₂ surface will increase by approximately one-third of the Cl atom spin-orbit splitting (that is, by 0.84 kcal/mol, bringing the overall barrier height on the BW surface up to 8.45 kcal/mol). The shape of the barrier may also change slightly because of the different angular dependences of the three coupled diabatic surfaces that correlate with Cl(²P) + H₂. This spin-orbit effect was not included in the present calculations, but recent thermal rate constant calculations for the Cl + H₂ reaction have shown, by including the effect as an energy shift, that the true barrier height is indeed likely to be close to 8.45 kcal/mol (U. Manthe, W. Bian, H.-J. Werner, *Chem. Phys. Lett.*, in press).
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Ordered Bicontinuous Nanoporous and Nanorelief Ceramic Films from Self Assembling Polymer Precursors

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Three-dimensional ceramic nanostructured films were produced from silicon-containing triblock copolymer films exhibiting the double gyroid and inverse double gyroid morphologies (space group *Im3d*). A one-step room-temperature oxidation process that used ozonolysis and ultraviolet irradiation effected both the selective removal of the hydrocarbon block and the conversion of the silicon-containing block to a silicon oxycarbide ceramic stable to 400°C. Depending on the relative volume fraction of the hydrocarbon block to the silicon-containing block, either nanoporous or nanorelief structures were fabricated with calculated interfacial areas of ~40 square meters per gram and pore or strut sizes of ~20 nanometers.

The controlled fabrication of mesoporous inorganic materials is an area of burgeoning interest because of their important applications as selective membranes, next-generation catalysts, and photonic materials. In 1993, Monnier *et al.* (1) reported the formation of mesoporous silica by using surfactant templates (MCM materials). This approach has allowed access to various mesoporous structures but generally involves multistep processes and does not allow simple production of large-area continuous films (2). Nonsurfactant templates, such as block copolymers or complex sugars, have also been used, but these processes again either involve multistep preparations (3), long processing times

such as drying for 15 to 20 days (4), high calcination temperatures (between 400° to 800°C) (5), or some combination of the above.

We have produced porous and relief ceramic nanostructures from self-assembling (template-free) block copolymer precursors, with a one-step, low-temperature technique. By careful selection of the relative volume fraction and phases, block copolymers can be used to produce precursor materials with a vast range of different symmetries and structures that allow nanostructures with highly ordered and complex pore or strut structures to be prepared (6). In addition, pore sizes, feature sizes, and spacings are also readily tailored either through blending of one or more homopolymers with the block copolymer or through control of molecular weight. A bifunctional oxidation process was used to both selectively remove a hydrocarbon block and convert a remaining silicon-containing block to a silicon oxycarbide ceramic. The resulting ceramic materials are either nanoporous [three-dimensional (3D) con-

nected pores] or nanorelief (3D connected strut networks), depending solely on the volume fraction of the hydrocarbon block relative to the silicon-containing block in the block copolymer precursor.

The formation of porous and relief nanostructures was accomplished by using two triblock copolymer precursors with compositions chosen to exhibit the double gyroid (7) and inverse double gyroid morphologies (space group *Im3d*) (Fig. 1). This morphology was chosen because it allowed the production of intricate ceramic nanostructures with periodicities in three dimensions that are not obtainable by conventional lithographic techniques because of the small size and complexity of the patterns formed. The materials are triblock copolymers of the type A₁BA₂, where A is polyisoprene (PI) and B is poly(pentamethyldisilylstyrene) [P(PMDSS)] (8, 9). One material has a composition of 24/100/26 (kg/mol) and forms a double gyroid morphology of PI networks [volume fraction of PI (ϕ_{PI}) = 33%] in a matrix of P(PMDSS) [referred to as the P(PMDSS)-DG] and is a precursor for the nanoporous structure. The other material has a composition of 44/168/112 (kg/mol) and forms the inverse double gyroid morphology of P(PMDSS) networks [$\phi_{P(PMDSS)}$ = 51%] in a matrix of PI [designated PI-DG] and can be converted into a nanorelief structure.

Samples of the triblock copolymers (1 mm thick) were cast from toluene and cryomicrotomed at -90°C. The approximately 50- to 100-nm-thick sections were then picked up either onto 600-mesh Cu grids or onto ultrathin amorphous carbon films on 100-mesh copper grids, and the PI blocks were preferentially stained in vapors of a 4% osmium tetroxide-water solution for 2 hours. These sections were then characterized in the bright-field mode with a JEOL 2000 FX transmission electron microscope (TEM), operating at 200 keV. Imaging of the unannealed, as-cast material revealed that highly ordered microphase separation occurs in this system even without annealing. Annealing the 1-mm-thick samples for 1 week at 120°C resulted in single grains that were several tens of

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square micrometers in area. Unstained sections of P(PMDSS)-DG supported on the carbon-coated Cu grids were exposed to a flowing 2% ozone atmosphere for 1 hour at room temperature. The PI-oxidized fragments were then removed by soaking the samples in deionized water overnight and the samples were examined by TEM.

Experimental TEM images of the double gyroid morphology for the P(PMDSS)-DG sample are oriented such that the viewing direction is approximately $[110]$. In Fig. 2A, the PI networks are preferentially stained with OsO_4 and appear darker than the surrounding P(PMDSS) matrix, whereas in Fig. 2B, the PI networks have been removed and appear lighter than the matrix, resulting in an inversion of the image contrast (10). The image periodicity of the ozone-treated sample is approximately the same as that of the unetched sample. The program TEMsim (11) was used to simulate a projection

of the morphology shown in Fig. 2C by assuming that the intermaterial dividing surface (the locus of largest gradient in sample composition), which defines the microdomain structure, can be approximated by a member of the gyroid level-set family of surfaces with $Ia3d$ symmetry and appropriate (34%) network volume fraction (12). The good correspondence of the TEM image (Fig. 2A) and simulation (Fig. 2C) is evident and allows the PI network strut diameter to be estimated as 20 nm. The specific surface can be estimated by using a level-set surface structure with 34 volume percent network component by computing the area per crystallographic unit cell using TEMsim and then scaling the dimensionless area $S/V^{2/3}$ to the actual size of the block copolymer unit cell. Small-angle x-ray scattering gave a d_{211} spacing of 49 nm, which yields the unit cell parameter as 120 nm. The interfacial area per gram of the nanoporous P(PMDSS)-DG material can thus be estimated

as $40 \text{ m}^2/\text{g}$, which is an order of magnitude less than that of common zeolites but quite high for a mesoscopic structure with a much larger interconnected pore size. Similarly, we can estimate the interfacial area per gram of the inverse double gyroid to be $36 \text{ m}^2/\text{g}$ based on the d_{211} of $\sim 62 \text{ nm}$ (from small-angle x-ray scattering) and the network volume fraction of 0.48.

Large-area nanoporous or nanorelief ceramic thin film samples (700 nm thick) were produced by spin-coating polymer solutions (4 to 6 weight %) in toluene at 4000 rpm onto Si(100) wafers coated with native oxide. Because these films have thicknesses much greater than the unit cell of the polymer, the bulk polygranular DG morphology was obtained for each copolymer. The spin-cast films were annealed for 2 days at 120°C and exposed to a stronger oxidation condition, which consisted of exposure to flowing 2% ozone atmosphere and 254-nm ultraviolet (UV) light (13) simultaneously for 1 hour (ozone + UV) and then soaked in deionized water overnight. Upon exposure to an oxidizing environment [either ozone and UV light or to an oxygen plasma (14)], the PI was removed and the silicon in the P(PMDSS) was converted to silicon oxycarbide.

The nanoporous and nanorelief morphologies of the spin-coated block copolymers subjected to ozone + UV were studied by atomic force microscopy (AFM) in an intermittent contact mode. Two types of structures were revealed. For the P(PMDSS)-DG, the PI networks have been selectively removed and the P(PMDSS) matrix converted to silicon oxycarbide to give an interconnected tortuous air network (Fig. 3) in a ceramic matrix that corresponds well to the feature sizes in the TEM micrographs of Fig. 2. Conversely, in the PI-DG sample, the PI matrix has been selectively

Fig. 1. Schematic of the crystallographic unit cell of the double gyroid morphology. The structure consists of two interpenetrating three-dimensionally continuous networks of the minority component, which are shown in green and blue to help in visualization. The networks are composed of cylinder-like connectors aligned along $\langle 110 \rangle$ directions joining in threes at nodes. There are 16 triple junction nodes per unit cell. For the P(PMDSS)-DG morphology, the networks are composed of PI and the matrix P(PMDSS), whereas for the inverse double gyroid morphology, PI-DG, the reverse is true. The figure was generated by surface rendering with a visual programming system (VPS).

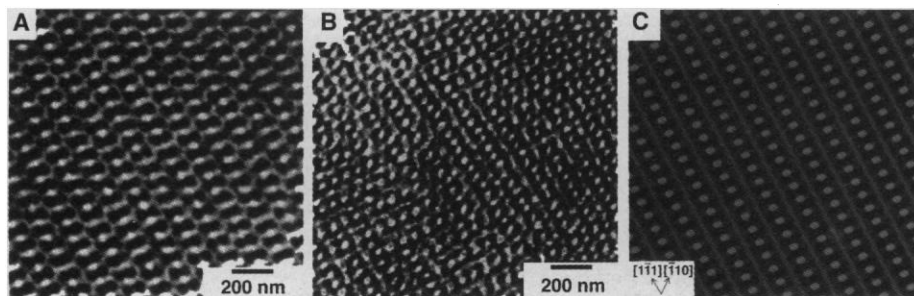
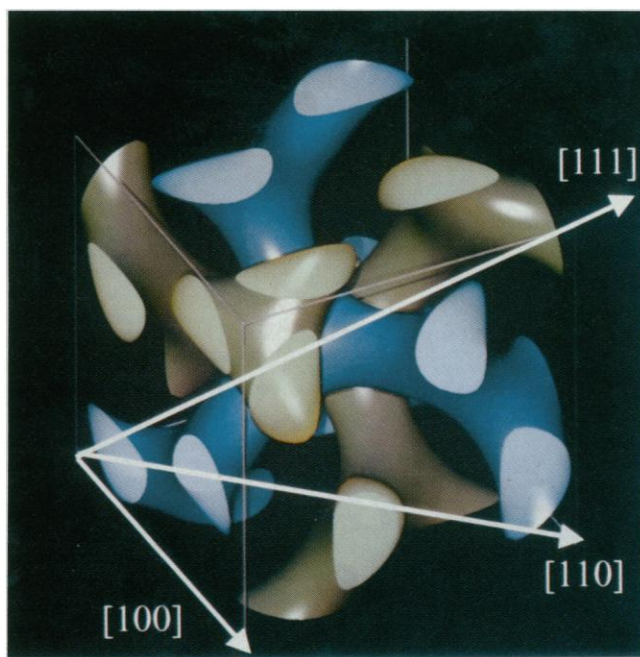


Fig. 2. Views along the $[110]$ direction of the P(PMDSS)-DG sample. (A and B) Bright-field TEM images of P(PMDSS)-DG. (A) OsO_4 -stained PI networks appear dark. (B) PI networks have been removed with ozone; as a result, the contrast has inverted and the networks appear light. (C) A TEM simulation of a projection down the $[110]$ exhibiting twofold symmetry. The networks are assigned a density of 1 and the P(PMDSS) matrix a density of 0. Section thickness is 40% of the repeat in the $[110]$ direction.

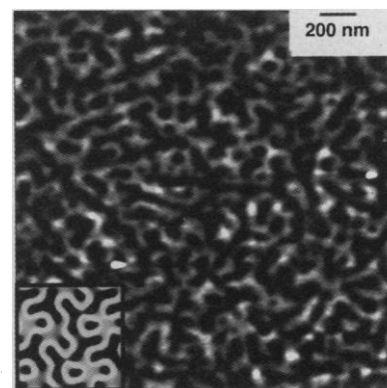


Fig. 3. An AFM image of surface topography of P(PMDSS)-DG after ozonolysis and UV exposure. The PI networks have been removed, resulting in the formation of ordered tortuous pathways within a silicon oxycarbide matrix. Bright regions are highest. Dark regions are empty. The maximum height on the image is 10 nm. (Inset) $[012]$ view at zero height of a volume-rendered surface of the double gyroid structure with empty strut networks, which appear dark.

removed to leave ceramic network struts to be imaged (Fig. 4A). This results in an inversion in the height contrast as compared with Fig. 3 because the networks rather than the matrix remain. Computer simulations of both porous and relief double gyroids were made using the hybrid volume/surface rendering component of TEMsim. The porous ceramic structure has a morphology similar to that of the double gyroid morphology viewed along the [012] direction at zero height (Fig. 3). Various areas of the relief double gyroid ceramic networks correlate well with simulated surface regions that have slightly different levels within the unit cell (Fig. 4B).

Ellipsometry, x-ray photoelectron spectroscopy (XPS), and Rutherford backscattering (RBS) studies on the P(PMDSS) homopolymer system (38 kg/mol) show that these oxidation conditions promote the conversion of the silicon-containing block to an oxycarbide (15). After exposing the P(PMDSS) homopolymer to ozone + UV for 1 hour, the refractive index changes from 1.56 to 1.42 (equal to that of SiO_2). The Si2p peak in XPS of the homopolymer shifts from 100.7 eV, which is the binding energy of Si in a hydrocarbon environment, to 103 eV, the binding energy of Si in SiO_2 (16). RBS confirmed that the stoichiometry of the film changed from that of P(PMDSS), $\text{Si}_1\text{O}_{0.7}\text{C}_{7.7}\text{H}_{11.3}$, to a silicon oxycarbide with a stoichiometry of $\text{Si}_1\text{O}_{1.6}\text{C}_{0.9}\text{H}_{1.6}$.

The ceramic that forms after oxidation should preferably exhibit high-temperature chemical and dimensional stability. After holding the ceramic film at 400°C for 1 hour in a nitrogen atmosphere, the film appears unchanged with only a slight decrease (<1%) in the refractive index and film thickness as deter-

mined by ellipsometry. In order to determine whether or not annealing changed the chemistry of the film, chemical analysis was performed by Auger electron spectroscopy. The atomic concentration and kinetic energy profiles for P(PMDSS) after exposure to ozone + UV and after annealing to 400°C for 1 hour in nitrogen are nearly indistinguishable. Indeed, after the 400°C anneal, the time to sputter to the interface remains the same (~2.2 min). In contrast, the untreated homopolymer film cracks and degrades at ~300°C to create a nonuniform and mottled surface (17). Thus, the low-temperature ozone + UV process produced an inorganic oxide with thermal stability properties far superior to those of the parent homopolymer (18). Because P(PMDSS) has been converted to a stable ceramic, the network struts in the nanorelief structures and matrix in the nanoporous structures will be stronger mechanically compared with the nonceramic struts that are left behind by ozonolysis alone, as in the case reported by Hashimoto *et al.* (19) and Lee *et al.* (20) for a nanoporous polymer structure.

In the search for routes to nanostructured materials, the process reported here is significant not only because of the type of materials that are attainable but because of the simplicity and versatility of the method: Large area, conformable, and continuous films and coatings can be produced; the precursor is an easily processible polymer; the nanostructures form by self-assembly without the need for a template; and the oxidation is done at room temperature with inexpensive equipment (21). The resulting class of materials could be used for applications where high-temperature stability, solvent resistance, or both are required. For

example, the P(PMDSS)-DG could be used as high-temperature nanoporous membranes with tailorable monodisperse interconnected pores with the added advantage that the redundancy of the interconnected pathways characteristic of the double gyroid structure substantially decreases the likelihood of the membrane being clogged by the filtrate (22). By varying the molecular weight, a range of pore sizes and specific areas can be obtained, presenting opportunities for separation and catalysis applications where larger component molecules are involved. Moreover, the ability to form continuous conformal coatings with high specific surface area presents opportunities for novel high-temperature catalytic applications. The ceramic network structure derived from the PI-DG copolymer has potential use in interconnects because of its low dielectric constant, high-temperature stability, and the inherent etch selectivity of this material to photoresist (23). These periodic and interconnected high dielectric/low dielectric ceramic/air structures also have potential as photonic band gap materials (24).

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9. The monomer (PMDSS) contains 24 weight % Si, which is much higher than the critical 10 weight % needed to form a coherent oxide when exposed to an oxygen plasma [E. Reichmanis and G. Smolinsky, *SPIE* **469**, 38 (1984)]. Because the silicon is intrinsically present in the monomer, the etch selectivity is also intrinsic in the block copolymer, so no postpolymerization chemistry is necessary, unlike hydrocarbon materials used previously by other groups [A. H. Gabor and C. K. Ober, *Microelectronics Technology: Polymers for Advanced Imaging and Packaging*, E. Reichmanis, Ed. (ACS Symposium Series 614, American Chemical Society, Washington, DC, 1995), chap. 19; M. Park, C. Harrison, P. M. Chaikin, R. A. Register, D. H. Adamson, *Science* **276**, 1401 (1997)].
10. For the PI-DG sample, unstained ozone-etched microtomed sections could not be imaged because upon soaking in deionized water, the thin section broke apart because of the fragility of the P(PMDSS) networks. However, if thicker, coherent films supported on silicon wafers are etched, the struts remain intact after removal of the matrix (15).
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13. UVP Pen-ray PCQ Lamp. Part number 90-0049-03. Lamp emits 8 mW/cm² 1.9 cm away from the light source.
14. Although oxidation by a plasma is also possible, the focus of this report is on the oxidation of this 3D block copolymer system using a room-temper-

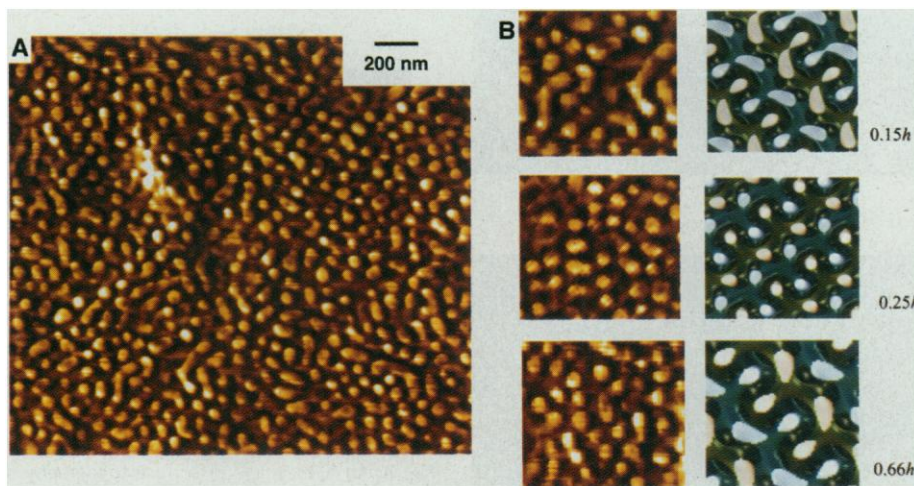


Fig. 4. (A) An AFM image of surface topography of PI-DG after ozonolysis and UV exposure. The PI matrix has been removed, leaving behind silicon oxycarbide networks. The highest regions are white and the lowest dark. The maximum z height in this image is 10 nm. (B) Enlargements of selected regions within (A). At the right are volume-rendered surfaces of the double gyroid morphology with silicon oxycarbide strut networks. The uppermost features are white. All simulations are [112] views of the DG silicon oxycarbide network structure with the surface at various heights within the unit cell (where the periodic repeat along [112], $h = \sqrt{6}a$). The matrix is made transparent to enable viewing of the networks.

- ature ozonolysis and UV process. Exposure to an oxygen plasma converts the P(PMDSS) to SiO_2 but the directionality of the plasma etch is problematic for the 3D double gyroid structure. A plasma asher that does not contain a forward bias or the use of higher gas pressures in the oxygen reactive ion etcher are ways to reduce the directionality of the plasma process.
15. P(PMDSS) homopolymer was spincoated from a 5 wt% solution in toluene onto Si(100) wafers. The solution was directly filtered onto the wafers by using a syringe equipped with a 0.2- μm filter. The samples were then annealed in a vacuum oven at 60°C to drive off excess toluene. The resulting thickness of these samples was 200 nm as measured by profilometry. The samples were then exposed to the same ozone + UV process (see above).
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25. We thank R. J. Composto and H. Wang for help with RBS experiments and P. Derege for helpful discussions. The NSF MRSEC shared experimental facilities at MIT were used. Funding was provided by Air Force Office of Scientific Research—ASSERT No. F49 620-94-1-0357, by the NSF Center for Polymer Interfaces and Macromolecular Assemblies (CPIMA) at IBM, and by NSF and IBM through graduate research fellowships for V.Z.-H.C., who also thanks S. Adams for inspiration.

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Single-Bond Formation and Characterization with a Scanning Tunneling Microscope

H. J. Lee and W. Ho*

A scanning tunneling microscope (STM) was used to manipulate the bonding of a carbon monoxide (CO) molecule and to analyze the structure and vibrational properties of individual products. Individual iron (Fe) atoms were evaporated and coadsorbed with CO molecules on a silver (110) surface at 13 kelvin. A CO molecule was transferred from the surface to the STM tip and bonded with an Fe atom to form Fe(CO). A second CO molecule was similarly transferred and bonded with Fe(CO) to form Fe(CO)₂. Controlled bond formation and characterization at the single-bond level probe chemistry at the spatial limit.

The ability to control chemistry at the spatial limit of individual atoms and molecules provides insights into the nature of the chemical bond and reactivity. As a step toward the realization of this goal, it is necessary to probe the properties of individual molecules and manipulate and alter their chemical composition.

The scanning tunneling microscope (STM) has been used to move and position single atoms (1–3) and molecules (4). The tip of the STM catalyzes surface reactions (5). Electrons tunneling through the electronic states of a molecule adsorbed on a surface also couple to intrinsic molecular motions such as rotation (4, 6) and vibration (7, 8), leading to the possibility of inducing chemical transformation in the molecule. Dissociation of single molecules has been accomplished on both metal (9) and semiconductor (10) surfaces. Although bond cleavage is central in chemical reactions, understanding the reverse process of bond formation, albeit a more difficult one to accomplish experimentally, is equally desirable.

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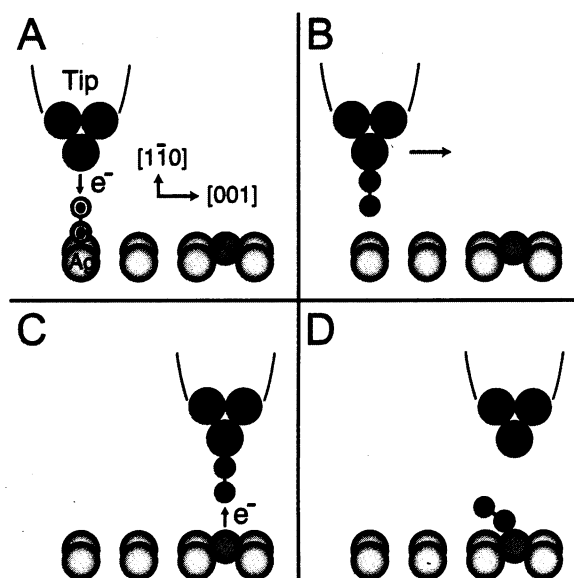
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Here, we used a low-temperature STM in an ultrahigh vacuum (11) to form a single bond and to characterize the reactants and products with spatial imaging and vibrational

spectroscopy. Starting with a clean Ag(110) surface at 13 K, individual Fe atoms were first evaporated onto the surface, and then CO molecules were coadsorbed from the gas phase. We limited exposures of Fe and CO to yield coverages of ~ 0.001 monolayer to circumvent interactions between coadsorbed species. With the STM, a single CO molecule was bonded to an Fe atom, thus making an Fe(CO) molecule on the surface. A second CO molecule could then be added to form Fe(CO)₂. The reactants and products were identified by their distinct STM images and vibrational energies.

The controlled formation of a Fe–CO bond with the STM consisted of a series of systematic steps (Fig. 1). The STM feedback remained on throughout the process. After taking a topographical image of the surface at 70-mV sample bias and 0.1-nA tunneling current, we positioned the tip over a CO molecule (Fig. 1A) adsorbed on top of a Ag

Fig. 1. Schematic diagrams showing the different steps in the formation of a single bond with the STM. The binding sites are determined by imaging the adsorbed species with a CO molecule attached to the tip (Fig. 4). The sizes of the circles are scaled to the atomic covalent radii. The polycrystalline tungsten tip is sputtered and annealed before use; physical contact is made with the Ag surface to further condition the tip. (A) The tip is positioned over a single CO molecule to induce the detachment of CO from Ag and its bonding to the tip. Because CO forms a bond predominantly through the carbon, a 180° rotation of the CO occurs in the transfer. (B) The tip with the attached single CO molecule is translated (indicated by the arrow) and positioned over an Fe atom. (C) The bias voltage and the flow of electrons are reversed, inducing the transfer of CO from the tip to the Fe. (D) A single Fe–CO bond is formed. The interaction of the electric field with the dipole moment of CO may also play a role in the transfer of (A) and (C).



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⁵ **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

Science, New Series, Vol. 279, No. 5350. (Jan. 23, 1998), pp. 548-552.

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⁹ **Block Copolymer Lithography: Periodic Arrays of similar to 10 ^{¹¹ Holes in 1 Square Centimeter}**

Miri Park; Christopher Harrison; Paul M. Chaikin; Richard A. Register; Douglas H. Adamson

Science, New Series, Vol. 276, No. 5317. (May 30, 1997), pp. 1401-1404.

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¹² **Triply Periodic Level Surfaces as Models for Cubic Tricontinuous Block Copolymer Morphologies**

Charla A. Lambert; Leonard H. Radzilowski; Edwin L. Thomas

Philosophical Transactions: Mathematical, Physical and Engineering Sciences, Vol. 354, No. 1715, Curved Surfaces in Chemical Structure. (Sep. 16, 1996), pp. 2009-2023.

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