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Chapter Title	Diamondoid Mechanosynthesis for Tip-Based Nanofabrication	
Chapter Sub-Title		
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Book Name	Tip-Based Nanofabrication	
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Abstract

Diamond mechanosynthesis (DMS), or molecular positional fabrication, is the formation of covalent chemical bonds using precisely applied mechanical forces to build nanoscale diamondoid structures via manipulation of positionally controlled tooltips, most likely in a UHV working environment. DMS may be automated via computer control, enabling programmable molecular positional fabrication. The Nanofactory Collaboration is coordinating a combined experimental and theoretical effort involving direct collaborations among dozens of researchers at institutions in multiple countries to explore the feasibility of positionally controlled mechanosynthesis of diamondoid structures using simple molecular feedstocks, the first step along a direct pathway to developing working nanofactories.

Keywords (separated by '-') Carbon placement - Diamond - Diamondoid - DMS - Hydrogen abstraction - Hydrogen donation - Mechanosynthesis - Minimal toolset - Molecular manufacturing - Nanofactory - Nanofactory Collaboration - Nanopart - Positional assembly - Positional fabrication - tooltips

Chapter 11
Diamondoid Mechanosynthesis for Tip-Based Nanofabrication

Robert A. Freitas Jr.

Abstract Diamond mechanosynthesis (DMS), or molecular positional fabrication, is the formation of covalent chemical bonds using precisely applied mechanical forces to build nanoscale diamondoid structures via manipulation of positionally controlled tooltips, most likely in a UHV working environment. DMS may be automated via computer control, enabling programmable molecular positional fabrication. The Nanofactory Collaboration is coordinating a combined experimental and theoretical effort involving direct collaborations among dozens of researchers at institutions in multiple countries to explore the feasibility of positionally controlled mechanosynthesis of diamondoid structures using simple molecular feedstocks, the first step along a direct pathway to developing working nanofactories.

Keywords Carbon placement · Diamond · Diamondoid · DMS · Hydrogen abstraction · Hydrogen donation · Mechanosynthesis · Minimal toolset · Molecular manufacturing · Nanofactory · Nanofactory Collaboration · Nanopart · Positional assembly · Positional fabrication · tooltips

Abbreviations

AFM	Atomic force microscope
CPU	Central processing unit
CVD	Chemical vapor deposition
DFT	Density functional theory
DMS	Diamond mechanosynthesis
DNA	Deoxyribonucleic acid
MEMS	Microelectromechanical systems
NIST	National Institute of Standards and Technology (U.S.)
NMAB	National Materials Advisory Board (U.S.)
NNI	National Nanotechnology Initiative (U.S.)
NRC	National Research Council of the National Academies (U.S.)
ONR	Office of Naval Research (U.S.)
SEM	Scanning electron microscopy

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A.A. Tseng (ed.), *Tip-Based Nanofabrication*, DOI 10.1007/978-1-4419-9899-6_11,

SPM	Scanning probe microscope
UHV	Ultra-high vacuum

11.1 Positional Diamondoid Molecular Manufacturing

Complex molecular machine systems [1–6], including microscale robotic mechanisms comprised of thousands or millions of nanoscale mechanical components such as gears, motors, and computer elements, probably cannot be manufactured using the conventional techniques of self-assembly. As noted in the final report [7] of the 2006 Congressionally-mandated review of the U.S. National Nanotechnology Initiative by the National Research Council (NRC) of the National Academies and the National Materials Advisory Board (NMAB): "For the manufacture of more sophisticated materials and devices, including complex objects produced in large quantities, it is unlikely that simple self-assembly processes will yield the desired results. The reason is that the probability of an error occurring at some point in the process will increase with the complexity of the system and the number of parts that must interoperate." Error detection and correction requires a minimum level of complexity that cannot easily be achieved via thermodynamically-driven self-assembly processes.

The opposite of self-assembly processes is positionally controlled processes, in which the positions and trajectories of all components of intermediate and final product objects are controlled at every moment during fabrication and assembly. Positional processes should allow more complex products to be built with high quality and should enable rapid prototyping during product development. Pure positional assembly is the norm in conventional macroscale manufacturing (e.g., cars, appliances, houses) but is only relatively recently [8, 9] starting to be seriously investigated experimentally for nanoscale manufacturing. Of course, we already know that positional fabrication can work in the nanoscale realm. This is demonstrated in the biological world by ribosomes, which positionally assemble proteins in living cells by following a sequence of digitally encoded instructions (even though ribosomes themselves are self-assembled). Lacking this positional fabrication of proteins controlled by DNA-based software, large, complex, digitally-specified organisms would probably not be possible and biology as we know it would not exist. Guided self-assembly – another hybrid approach combining self-assembly and positional assembly – is also being investigated experimentally [10, 11].

The most important materials for positional assembly may be the rigid covalent or "diamondoid" solids, since these could potentially be used to build the most reliable and complex nanoscale machinery. Preliminary theoretical studies have suggested great promise for these materials in molecular manufacturing. The NMAB/NRC Review Committee recommended [7] that experimental work aimed at establishing the technical feasibility of positional molecular manufacturing should be pursued and supported: "Experimentation leading to demonstrations supplying ground truth for abstract models is appropriate to better characterize the potential for use of bottom-up or molecular manufacturing systems that utilize processes more complex than self-assembly." Making complex nanorobotic systems requires manufacturing techniques that can build a molecular structure by positional assembly [9, 12]. This will involve picking and placing molecular parts one by one, moving them along controlled trajectories much like the robot arms that manufacture cars on automobile assembly lines. The procedure is then repeated over and over with all the different parts until the final product is fully assembled inside a desktop nanofactory.

Technologies required for the atomically precise fabrication of diamondoid nanorobots in macroscale quantities at low cost requires the development of a new nanoscale manufacturing technology called positional diamondoid molecular manufacturing, enabling diamondoid nanofactories. Achieving this new technology over the next 1–3 decades will require the significant further development of multiple closely related technical capabilities: diamondoid mechanosynthesis, programmable positional assembly, massively parallel positional fabrication and assembly, and nanomechanical design.

11.2 Diamondoid Mechanosynthesis (DMS)

Mechanosynthesis, or molecular positional fabrication, is the formation of covalent chemical bonds using precisely applied mechanical forces to build atomically precise structures. Mechanosynthesis will be most efficient when automated via computer control, enabling programmable molecular positional fabrication of nanostructures of significant size. Atomically precise fabrication involves holding feedstock atoms or molecules, and separately a growing nanoscale workpiece, in the proper relative positions and orientations so that when they touch they will chemically bond in the desired manner. In this process, a mechanosynthetic tool is brought up to the surface of a workpiece. One or more transfer atoms are added to (Fig. 11.1), or removed from, the workpiece by the tool. Then the tool is withdrawn and recharged. This process is repeated until the workpiece (e.g., a growing nanopart) is completely fabricated to atomic precision with each atom in exactly the right place. The transfer atoms are under positional control at all times to prevent unwanted side reactions from occurring. Side reactions are also avoided using proper reaction design so that the reaction energetics avoid undesired pathological intermediate structures and atomic rearrangements.

The positional assembly of diamondoid structures, some almost atom by atom, using molecular feedstock has been examined theoretically [13–25] via computational models of diamondoid mechanosynthesis (DMS). DMS is the controlled addition of individual carbon atoms, carbon dimers (C_2), or single methyl (CH_3) and like groups to the growth surface of a diamond crystal lattice workpiece in an inert manufacturing environment such as UHV. Covalent chemical bonds are formed one by one as the result of positionally constrained mechanical forces applied at the tip of a scanning probe microscope (SPM) apparatus, usually resulting in the addition of one or more atoms having one or more bonds into the workpiece structure.

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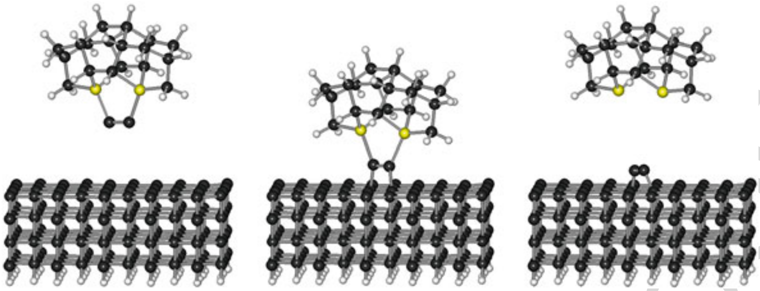

Fig. 11.1 Diamondoid mechanosynthesis: DCB6Ge dimer placement tool shown depositing two carbon atoms on a diamond surface (C = *black*, H = *white*, Ge = *yellow/gray*) [9]. © 2010 Robert A. Freitas Jr. All Rights Reserved

Programmed sequences of carbon dimer placement on growing diamond surfaces in vacuo appear feasible in theory [20, 24].

11.2.1 Diamondoid Materials

Diamondoid materials include pure diamond, the crystalline allotrope of carbon. Among other exceptional properties, diamond has extreme hardness, high thermal conductivity, low frictional coefficient, chemical inertness, a wide electronic bandgap, and is the strongest and stiffest material presently known at ordinary pressures. Diamondoid materials also may include any stiff covalent solid that is similar to diamond in strength, chemical inertness, or other important material properties, and possesses a dense three-dimensional network of bonds. Examples of such materials are carbon nanotubes and fullerenes, atomically-precise doped diamond, several strong covalent ceramics such as silicon carbide, silicon nitride, and boron nitride, and a few very stiff ionic ceramics such as sapphire (monocrystalline aluminum oxide) that can be covalently bonded to pure covalent structures such as diamond. Of course, pure crystals of diamond are brittle and easily fractured. The intricate molecular structure of an atomically precise diamondoid product will more closely resemble a complex composite material, not a brittle solid crystal. Such products, and the nanofactory systems that build them, should be extremely durable in normal use.

11.2.2 Minimal Toolset for DMS

It is already possible to synthesize bulk diamond today. In a process somewhat reminiscent of spray painting, layer after layer of diamond is built up by holding a cloud of reactive hydrogen atoms and hydrocarbon molecules over a deposition surface. When these molecules bump into the surface they change it by adding, removing, or rearranging atoms. By carefully controlling the pressure, temperature, and the exact composition of the gas in this process – called chemical vapor deposition or CVD – conditions can be created that favor the growth of diamond on the surface. But randomly bombarding a surface with reactive molecules does not offer fine control over the growth process. To achieve atomically precise fabrication, the first challenge is to make sure that all chemical reactions will occur at precisely specified places on the surface. A second problem is how to make the diamond surface reactive at the particular spots where we want to add another atom or molecule. A diamond surface is normally covered with a layer of hydrogen atoms. Without this layer, the raw diamond surface would be highly reactive because it would be studded with unused (or "dangling") bonds from the topmost plane of carbon atoms. While hydrogenation prevents unwanted reactions, it also renders the entire surface inert, making it difficult to add carbon (or anything else) to this surface.

To overcome these problems, a set of molecular-scale tools must be developed that would, in a series of well-defined steps, prepare the surface and create hydrocarbon structures on a layer of diamond, atom by atom and molecule by molecule. A mechanosynthetic tool typically will have two principal components – a chemically active tooltip and a chemically inert handle to which the tooltip is covalently bonded. The tooltip is the part of the tool where site-specific single-molecule chemical reactions are forced to occur by the application of mechanical energy. The much larger handle structure is big enough to be grasped or positionally manipulated using an SPM or similar macroscale instrumentality. At least three types of basic mechanosynthetic tools (Fig. 11.2) have already received considerable theoretical (and some related experimental) study and are likely among those required to build molecularly precise diamond via positional control:

(1) *Hydrogen Abstraction Tools*. The first step in the process of mechanosynthetic fabrication of diamond might be to remove a hydrogen atom from each of two specific adjacent spots on the diamond surface, leaving behind two reactive dangling bonds. This could be done using a hydrogen abstraction tool [21] (Fig. 11.2a) that has a high chemical affinity for hydrogen at one end but is elsewhere inert. The tool's unreactive region serves as a handle or handle attachment

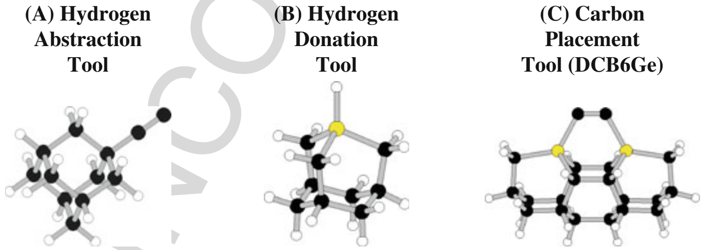

Fig. 11.2 Examples of three basic mechanosynthetic tooltypes that are required to build atomically precise diamond via positional control (C = *black*, H = *white*, Ge = *yellow/gray*) [24]. © 2007 Robert A. Freitas Jr. All Rights Reserved

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point. The tool would be held by a high-precision nanoscale positioning device, initially perhaps a scanning probe microscope tip but ultimately a molecular robotic arm, and moved directly over particular hydrogen atoms on the surface. One suitable molecule for a hydrogen abstraction tooltip is the acetylene or "ethynyl" radical, comprised of two carbon atoms triple bonded together. One carbon of the two serves as the handle connection, and would bond to a nanoscale positioning device through a larger handle structure. The other carbon of the two has a dangling bond where a hydrogen atom would normally be present in a molecule of ordinary acetylene (C_2H_2), which can bond and thereby abstract a hydrogen atom from a workpiece structure. The environment around the tool would be inert (e.g., vacuum or a noble gas such as neon). The first extensive DMS tooltip trajectory analysis, examining a wide range of viable multiple degrees-of-freedom tooltip motions in 3D space that could be employed in a separate reaction sequence to recharge the ethynyl-based hydrogen abstraction tool (Fig. 11.3), was published in 2010 [25].

(2) *Carbon Placement Tools*. After the abstraction tool has created adjacent reactive spots by selectively removing hydrogen atoms from the diamond surface but before the surface is re-passivated with hydrogen, carbon placement tools may be used to deposit carbon atoms at the desired reactive surface sites. In this way a diamond structure can be built up on the surface, molecule by molecule, according to plan. The first complete tool ever proposed for this carbon deposition function is the "DCB6Ge" dimer placement tool [15] – in this example, a carbon (C_2) dimer having two carbon atoms connected by a triple bond with each carbon in the dimer connected to a larger unreactive handle structure via two germanium atoms (Fig. 11.2c). This dimer placement tool, also held by a nanoscale positioning device, is brought close to the reactive spots along a particular trajectory, causing the two dangling surface bonds to react with the ends of the carbon dimer. The dimer placement tool would then withdraw, breaking the relatively weaker bonds between it and the C_2 dimer and transferring the carbon dimer from the tool to the surface. A positionally controlled dimer could be bonded at many different sites on a growing diamondoid workpiece, in principle allowing the construction of a wide variety of useful nanopart

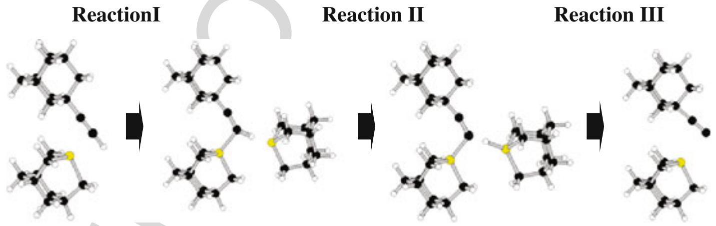

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Fig. 11.3 Schematic of recharge reaction for 1-ethynyladamantane hydrogen abstraction tool (end product of Reaction III, structure at top) using sequence of three positionally controlled reactions involving two 1-germanoadamantane radical tooltips (C = *black*, H = *white*, Ge = *yellow/gray*) [25]. © 2008 Robert A. Freitas Jr. All Rights Reserved shapes. As of 2010, the DCB6Ge dimer placement tool remains the most studied [15, 17, 19, 20, 22, 24] of any mechanosynthetic tooltip to date, having had more than 150,000 CPU-hours of computation invested thus far in its analysis, and it remains the only tooltip motif that has been successfully simulated and theoretically validated for its intended function on a full 200-atom diamond workpiece surface [20]. Other proposed dimer (and related carbon transfer) tooltip motifs [13–15, 18, 22, 24] have received less intensive study but are also expected to perform well.

(3) *Hydrogen Donation Tools*. After an atomically precise structure has been fabricated by a succession of hydrogen abstractions and carbon depositions, the fabricated structure must be passivated to prevent additional unplanned reactions. While the hydrogen abstraction tool is intended to make an inert structure reactive by creating a dangling bond, the hydrogen donation tool [23] does the opposite (Fig. 11.2b). It makes a reactive structure inert by terminating a dangling bond by adding an H atom. Such a tool would be used to stabilize reactive surfaces and help prevent the surface atoms from rearranging in unexpected and undesired ways. The key requirement for a hydrogen donation tool is that it include a weakly attached hydrogen atom. Many molecules fit that description, but the bond between hydrogen and germanium is sufficiently weak so that a Ge-based hydrogen donation tool should be effective.

A 3-year study [24] representing 102,188 CPU hours of computing effort for the first time computationally analyzed a comprehensive set of DMS reactions and an associated minimal set of nine specific DMS tooltips that could be used to build basic diamond, graphene (e.g., carbon nanotubes), and all of the tools themselves including all necessary tool recharging reactions. The research defined 65 DMS reaction sequences incorporating 328 reaction steps, with 354 pathological side reactions analyzed and with 1,321 unique individual DFT-based (Density Functional Theory) quantum chemistry reaction energies reported. These mechanosynthetic reaction sequences range in length from 1 to 13 reaction steps (typically 4) with 0–10 possible pathological side reactions or rearrangements (typically 3) reported per reaction.

The first practical proposal for building a DMS tool experimentally was published in 2005 [19] and is the subject of the first diamond mechanosynthesis patent ever issued (in 2010) [19]. According to the original proposal, the manufacture of a complete "DCB6Ge" positional dimer placement tool would require four distinct steps: synthesizing a capped tooltip molecule, attaching it to a deposition surface, attaching a handle to it via CVD, then separating the tool from the deposition surface. An even simpler practical proposal for building DMS tools experimentally, also using only experimental methods available today, was published in 2008 as part of the aforementioned minimal toolset work [24]. Processes were identified for the experimental fabrication of a hydrogen abstraction tool, a hydrogen donation tool, and two alternative carbon placement tools (other than DCB6Ge). These processes and tools are part of the second mechanosynthesis patent ever filed and provide clear developmental targets for a comprehensive near-term DMS implementation program to begin working toward a more mature set of efficient, positionally controlled mechanosynthetic tools that can reliably build atomically precise diamondoid structures – including more DMS tools.

11.2.3 Experimental Activities to Date

The first experimental proof that individual atoms could be manipulated was obtained by IBM scientists in 1989 when they used a scanning tunneling microscope to precisely position 35 xenon atoms on a nickel surface to spell out the corporate logo "IBM". However, this feat did not involve the formation of covalent chemical bonds. One important step toward the practical realization of DMS was achieved in 1999 [26] with the first site-repeatable site-specific covalent bonding operation of a two diatomic carbon-containing molecules (CO), one after the other, to the same atom of iron on a crystal surface, using an SPM.

The first experimental demonstration of true mechanosynthesis, establishing covalent bonds using purely mechanical forces in UHV – albeit on silicon atoms, not carbon atoms – was reported in 2003 [27]. In this landmark experiment, the researchers vertically manipulated single silicon atoms from the Si(111)-(7×7) surface, using a low-temperature near-contact atomic force microscope to demonstrate: (1) removal of a selected silicon atom from its equilibrium position without perturbing the (7×7) unit cell, and (2) the deposition of a single Si atom on a created vacancy, both via purely mechanical processes. The same group later repeated this feat with Ge atoms [28]. By 2008, the Custance group in Japan [29] had progressed to more complex 2D structures fabricated entirely via mechanosynthesis using more than a dozen Si/Sn or Pb/In atoms [29], with a 12-atom 2D pattern created in 1.5 h (∼450 s/atom). In late 2008 Moriarty's group at the University of Nottingham (U.K.) began a $3 million 5-year effort [30] employing a similar apparatus to produce 2D patterns using carbon atoms, to validate the theoretical DMS proposals of Freitas and Merkle [24]. If successful, Moriarty's work may lead to subsequent studies extending DMS from 2D to small 3D carbon nanostructures.

Positional control and reaction design are key for the success of DMS. Error correction will be difficult or even impossible in many cases, so each reaction must be executed precisely on the first attempt. To accomplish this, sequences of positionally controlled reaction steps must be chosen such that desired reactions are energetically favored, side reactions or other undesired reactions are energetically disfavored, and defect formation or unwanted lattice rearrangements are either energetically disfavored or blocked by sufficient barriers to prevent their occurrence. Reaction sequences for building diamond and fullerene nanostructures that appear to meet these requirements have been proposed theoretically [24] and are now being investigated experimentally [30].

An extensive bibliography of theoretical and experimental work on DMS is available at http://www.MolecularAssembler.com/Nanofactory/AnnBibDMS.htm.

11.3 Programmable Positional Fabrication and Assembly

After demonstration of basic DMS, the next major experimental milestone may be the mechanosynthetic fabrication of atomically precise 3D structures, creating readily accessible diamondoid-based nanomechanical components engineered to form desired architectures possessing superlative mechanical strength, stiffness, and strength-to-weight ratio. These nanoscale components may range from relatively simple diamond rings, rods and cubes [31] to more sophisticated “nanoparts” such as fullerene bearings [32–34], gears [35–37] and motors [38], composite fullerene/diamond structures [39], and more complex devices [13] such as diamondoid gears [40], pumps [40], and conveyors [41].

Atomically precise nanoparts, once fabricated, must be transferred from the fabrication site and assembled into atomically precise complex components containing many nanoparts. Such components may include gear trains in housings [42], sensors, motors, manipulator arms, power generators, and computers. These complex components may then be assembled, for example, into an even more complex molecular machine system that consists of many complex components. A micron-size medical nanorobot such as a respirocyte [1] constructed of such molecularly precise components may possess many tens of thousands of individual components, millions of primitive nanoparts, and many billions of atoms in its structure. The conceptual dividing line between fabrication and assembly may sometimes become blurred because in many cases it might be possible, even preferable, to fabricate nominally multipart components as a single part – allowing, for example, two meshed gears and their housing to be manufactured as a single sealed unit.

The process of positional assembly, as with DMS, can be automated via computer control as has been demonstrated experimentally in the case of individual atoms in the Autonomous Atom Assembly project sponsored by NIST and ONR [43], in the case of nanoscale objects in SEM [44, 45] and AFM-based [45–47] manipulation systems, and in the case of microscale parts in automated MEMS assembly [48, 49]. This capability will allow the design of positional assembly stations [46, 47] which receive inputs of primitive parts and assemble them in programmed sequences of steps into finished complex components. These components can then be transported to secondary assembly lines which use them as inputs to manufacture still larger and more complex components, or completed systems, again analogous to automobile assembly lines.

For nanofactories to be economically viable, we must also be able to assemble complex nanostructures in vast numbers – in billions or even trillions of finished units (product objects). Approaches under consideration include using replicative manufacturing systems or massively parallel fabrication, employing large arrays of scanning probe tips all building similar diamondoid product structures in unison, as in nanofactories [9, 13, 50]. This will require massively parallel manufacturing systems with millions of assembly lines operating simultaneously and in parallel, not just one or a few of them at a time as with the assembly lines in modern-day car factories. Fortunately, each nanoassembly production line in a nanofactory can, in principle, be quite small. Many millions of them should easily fit into a very small volume. Massively parallel manufacture of DMS tools, handles, and related nanoscale fabrication and assembly equipment will also be required, perhaps involving the use of massively parallel manipulator arrays or some other type of replicative system [50].

Reliability is an important design issue. The assembly lines of massively parallel manufacturing systems might have numerous redundant smaller assembly lines feeding components into larger assembly lines, so that the failure of any one smaller line cannot cripple the larger one. Arranging parallel production lines for maximum efficiency and reliability to manufacture a wide variety of products (possibly including error detection, error correction and removal of defective parts) is a major requirement in nanofactory design.

Computational tools for molecular machine modeling, simulation and manufacturing process control must be created to enable the development of designs for diamondoid nanoscale parts, components, and nanorobotic systems. These designs can then be rigorously tested and refined in simulation before undertaking more expensive experimental efforts to build them. Molecular machine design and simulation software is available [42] and libraries of predesigned nanoparts are slowly being assembled. More effort must be devoted to large-scale simulations of complex nanoscale machine components, design and simulation of assembly sequences and manufacturing process control, and general nanofactory design and simulation.

11.4 Nanofactory Collaboration

The NMAB/NRC Review Committee, in their Congressionally-mandated review [7] of the NNI, called for proponents of "site-specific chemistry for large-scale manufacturing" to: (1) delineate desirable research directions not already being pursued by the biochemistry community; (2) define and focus on some basic experimental steps that are critical to advancing long-term goals; and (3) outline some "proof-of-principle" studies that, if successful, would provide knowledge or engineering demonstrations of key principles or components with immediate value.

In direct response to these requirements, the Nanofactory Collaboration [9] is coordinating a combined experimental and theoretical effort to explore the feasibility of positionally controlled mechanosynthesis of diamondoid structures using simple molecular feedstock. The precursor to the Nanofactory Collaboration was informally initiated by Robert Freitas and Ralph Merkle in the Fall of 2000 during their time at Zyvex. Their continuing efforts, and those of others, have produced direct collaborations among 25 researchers or other participants (including 18 PhD's or PhD candidates) at 13 institutions in 4 countries (U.S., U.K., Russia, and Belgium), as of 2010. The Collaboration website is at http://www.MolecularAssembler.com/Nanofactory.

At present, the Collaboration is a loose-knit community of scientists and others who are working together as time and resources permit in various team efforts with these teams producing numerous co-authored publications, though with disparate funding sources not necessarily tied to the Collaboration. While not all participants may currently envision a nanofactory as the end goal of their present research (or other) efforts in connection with the Collaboration, many *do* envision this, and even those who do not currently envision this end goal have nonetheless agreed to do research in collaboration with other participants that we believe will contribute important advances along the pathway to diamondoid nanofactory development, starting with the direct development of DMS. While some work has been done on each of the multiple capabilities believed necessary to design and build a functioning nanofactory, for now the greatest research attention is being concentrated on the first key area: proving the feasibility, both theoretical and experimental, of achieving diamondoid mechanosynthesis. We welcome new participants who would like to help us address the many remaining technical challenges [51] to the realization of a working diamondoid nanofactory.

Acknowledgments The author acknowledges private grant support for this work from the Life Extension Foundation, the Kurzweil Foundation, and the Institute for Molecular Manufacturing.

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Chapter 11

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