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DNA as a Nanomaterial

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Abstract—This review discusses information about the use of DNA as a basis for preparing materials with new properties. The unique molecular recognition property of nucleic acids that underlies the synthesis of targeted controllable structures, where DNA functions as an engineering material rather than a genetic-information carrier, is considered. Causes of significant advances in this field are discussed. The new functional potential of novel materials is examined.

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Since it was discovered that nucleic acids (NAs) are the carriers of genetic information of living cells, abundant information has been accumulated about the structural features of NAs and the feasible interaction between their bases. Automatic synthesizers of NAs have been developed. As a result, any nucleotide sequence of a desired composition with incorporation of additional modifications or without them can be synthesized under laboratory conditions. Owing to the rapid development of nucleic acid chemistry, these compounds have found use as a basis for new materials. A new concept, DNA nanotechnology, has been launched [1]. This branch of science endeavors to use unique molecular recognition properties of nucleic acids in order to obtain targeted controllable two- or three-dimensional structures, that is, to use DNA as an engineering material rather than a genetic information carrier.

The intense development of DNA nanotechnology is related to the emergence of new functional applications of DNA, for example, making parallel calculations on its basis. Other examples illustrating the advantageous use of DNA to serve a new function are the simultaneous detection of several parameters and the decision about the release of drugs at the level of the living cell. Of prime interest are the unusual properties of new materials based on DNA. The dynamic patterning of the structure of such materials, the programmable multistage chemical synthesis, the targeted stereospecificity of reactions, and the creation of nanoscale structures that are responsive to their environments become possible. The goal of this review is to consider the potential of DNA as a basis for the creation of new materials.

The key property of DNA underlying the creation of new DNA-based materials is its self-assembly ability. Molecular self-assembly is a process in which molecules interact with each other and assume a certain spatial arrangement without any external control. The appearance of such complexes in the case of DNA may be predicted on the basis of knowledge about hydrogen bonds between bases of nucleic acids and the spatial organization of NAs. DNA is a polymer composed of units—nucleotides—connected in a certain manner (Fig. 1). A nucleotide consists of a carbohydrate residue, a heterocyclic base forming a nucleoside, and a phosphate group. An NA contains bases of two kinds: purines and pyrimidines (Fig. 1a). The primary structure of an NA is determined by the sequence of nucleotide units linked via phosphodiester bonds (Fig. 1b). The macromolecular (secondary, tertiary) structure of an NA is the spatial organization of polynucleotide chains that is primarily controlled by the interaction between bases of various nucleotides via hydrogen bonding (Fig. 1c). The diversity of these structures is associated with the possibility to form various kinds of hydrogen bonds between heterocyclic bases. The main type of this interaction (formation of hydrogen bonds between purine and pyrimidine) is referred to as a Watson–Crick interaction (Fig. 1c). This interaction occurs in antiparallel duplexes. The secondary structure of DNA is a double helix that is stabilized by Watson–Crick and stacking interactions between base pairs (Fig. 1d). The same geometry of A–T and G–C pairs provides formation of DNA duplexes whose structure is regular and insignificantly dependent on nucleotide composition. Polymorphism of the double helix is possible for different nucleotide sequences and external conditions. More comprehensive information about the structure and properties of nucleic acids is available in the manual by Shabarova and Bogdanov [2]. An external impetus may stimulate a change in the spatial structure of DNA, that is, the transition from a single-stranded structure to a double-standed structure. At the structural level, an external impetus may stimulate the coil-to-rod transition (Fig. 2d), which

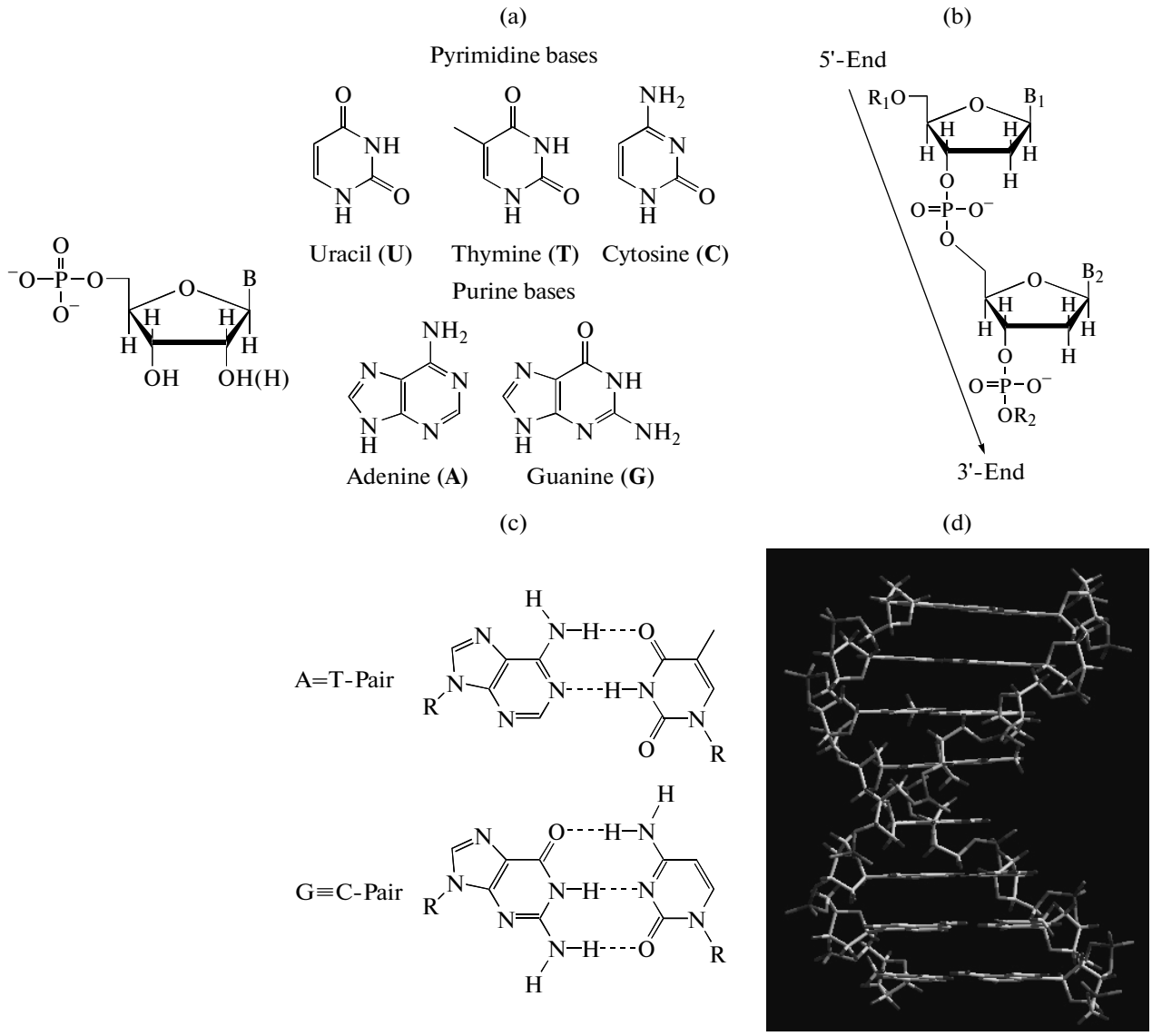

Fig. 1. (a) NA monomers, (b) internucleotide bond, (c) Watson–Crick base pairs, and (d) spatial scheme of the double helix. Here, B_1 and B_2 are schematic designations of bases.

depends on the amount of A–T and G–C pairs in the duplex, the length of the duplex, and external conditions. During programming of self-assembly routes, feasible noncanonical structures of NAs different from the double helix structure, namely, quadruplexes [3] and triplexes [4], should be taken into account as well. Moreover, in recent years, *L*-DNA–the mirror image of natural *D*-DNA–has been used in DNA nanotechnology. The use of enantiomeric DNA as a building block leads to formation of structures with opposite chirality properties. *L*-DNA, which is capable of self-assembly, shows stability against nucleases; therefore, its use is attractive for creation of medical materials [5].

Another use of DNA different from the transfer of genetic information was suggested a long time ago. In 1994, computer scientist Leonard Adleman proposed that the complementarity of DNA may be useful for solving complex mathematical problems. Adleman succeeded in solving the Hamiltonian Path problem (known also as the traveling salesman problem) with the use of DNA. This goal of the problem is to find the shortest route between all points—cities—that goes through each city only once [6]. Each city was encoded as a unique DNA sequence, and each path between two cities was encoded as a sequence complementary to a half-unique DNA sequence of each of these cities. During solution cooling, all sequences interacted to form new double helices. In theory, the solution to this problem was one of the new double strands: the shortest one that contains sequences of all

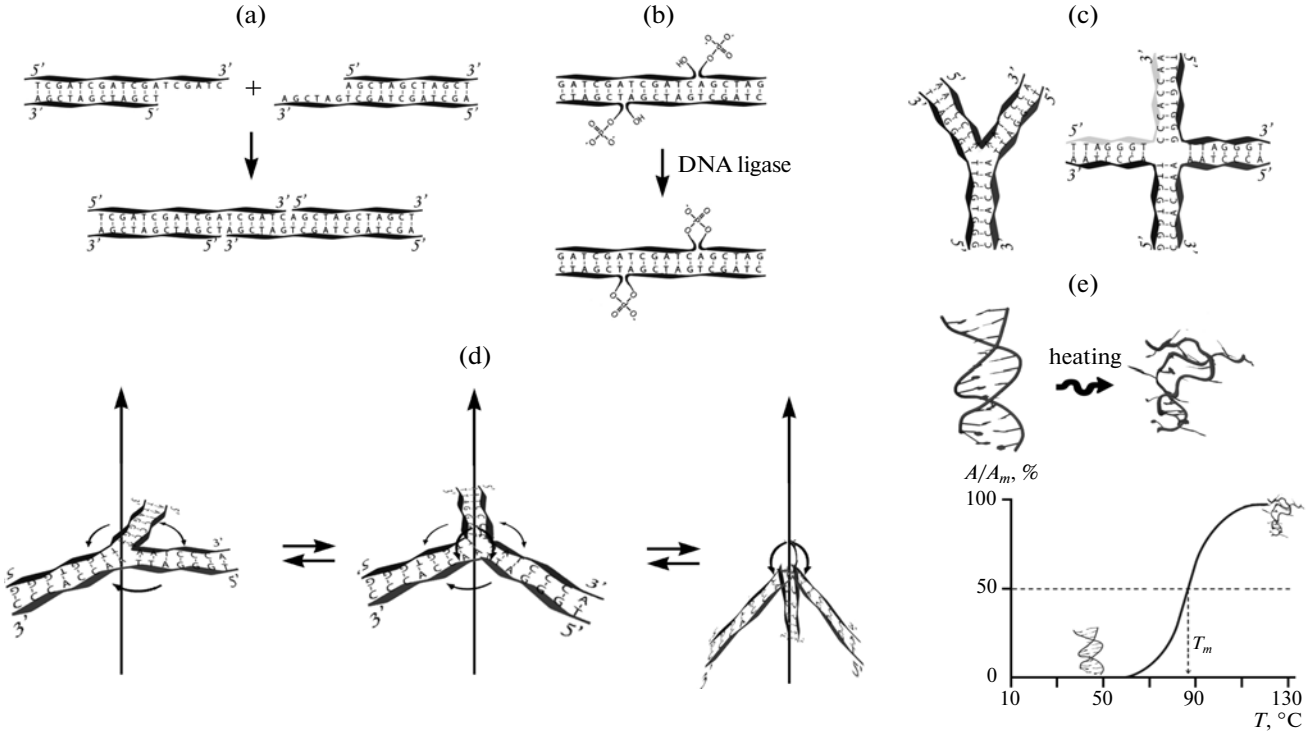

Fig. 2. (a) Interaction of helices with an extended end, (b) scheme of internucleotide-bond recovery (ligation), (c) Y- and X-shaped DNA blocks, (d) schematic representation of DNA-junction mobility, (e) curve of DNA melting, and rod–coil transition.

cities. The proper solution was found via elimination with the use of physical methods for separating NAs.

The key advantage of creation and use of DNA computers is that complex problems may be solved owing to generation of all possible solutions at one time. This method is known as parallel data processing. Humans and most electronic computers take on tasks one at a time (linear processing). The hope is to fit more than 10 trillion DNA molecules into an area no larger than 1 cm^3. Thus, a DNA computer would be able to hold 10 terabytes of data and perform 10 trillion calculations at a time. Another advantage of DNA computers is that such systems may be used in biological liquids [7]. The first simple computer language at the molecular scale was offered in [8]. However, further progress in this direction was restrained by certain technical difficulties related to the selection of proper solutions.

DNA may be used as a material both for making surfaces with repeating or random patterns and for assembling three-dimensional structures. The design of regular surfaces based on DNA relies on the use of preformed blocks. Oligonucleotide sequences are selected for synthesis in such a manner that one sequence will contain several portions complementary to other sequences. (In Fig. 2c, each sequence is complementary to two other sequences.) Three such sequences form a Y-shaped or three-arm junction, and four sequences form an X-shaped or four-arm junction. The junction ensures the flexibility of the block (Fig. 2d), and "arms" (double helix portions) provide rigidity to the block. The targeted assembly of blocks is possible because double helices contain extended single-stranded ends that can form a double helix between them in accordance with the complementarity principle (Fig. 2a). The direct formation of a new material occurs after recovery of a phosphodiester bond between two adjacent bases of the double helix (Fig. 2b). This reaction is catalyzed by the DNA ligase enzyme in the presence of adenosine triphosphate. The formed bond is covalent; as a result, the constructed material is stable against external stimuli: heating, high concentrations of salts, etc. If the same enzyme is added to a solution containing blocks without extended ends (i.e., all ends are compatible with each other), a hydrogel appears. This three-dimensional material with a controlled size of pores is characterized by biodegradability, and the rate of its biodegradation is structure-dependent. This material may be of use as a container for drugs [9]. Of special note is the biocompatibility of such hydrogels, which allows for incorporation of animal cells into them and their further cultivation. The advancement of studies in this field will lead to the three-dimensional cultivation of cells required for tissue engineering and cellular therapy [9]. Preformed blocks with alternating sticky ends

are suitable for the synthesis of extended planar surfaces with a regular relief [10] and lattices [11]. Figure 3b illustrates the formation of a DNA network. Blocks may be amplified via placement of additional duplexes in the desired site of the surface [12]. Depending on the alternation of sequences comprising the block, DNA ribbons of various widths may be assembled. When the hexagonal basis was used, ribbons 20 and 40 nm in width were constructed [13]. A change in the surface may be programmed in advance; for example, new single-stranded ends may be predesigned owing to introduction of a specific endonuclease (a sequence specifically recognized by an enzyme that cleaves the internucleotide bond) recognition site or owing to incorporation of DNA self-cleaving sequences (DNAzymes), which exhibit activity in the presence of certain metal ions [14]. This phenomenon makes it possible to change the surface structure.

Let us consider the possible use of the surface of DNA as a support for the assembly of complexes and a basis for the spatial arrangement of other nanoparticles. For this purpose, various objects (biomolecules, metal nanoparticles, etc.) are additionally modified with a single-stranded DNA adaptor. The nucleotide sequence of the adaptor determines to which location of the surface this structure will be attached. Extended free single-stranded regions (Fig. 3c) able to form a double helix are planned in advance on the DNA surface. Positioning due to formation of the double helix between the nano-object adaptor and the single-stranded region of the DNA surface makes it possible to study spatially dependent interactions between different structures, for example, biomolecules and ligands, or allows self-organization of complex cascades of multienzymes catalyzing consecutive transformations of substances. In [15], the final yield of two consecutive reactions catalyzed successively by glucose oxidase and horseradish peroxidase depended on the distance at which these two enzymes were anchored on the DNA surface. The arrangement of other nanoparticles in space may be illustrated by the block assembly of the DNA surface based on the four-arm element (this block has its own natural analog, the so-called Holliday junction) with regularly extending free single-stranded portions ensuring the fit of metal nanoparticles (in Fig. 3c, balls denote metal nanoparticles) conjugated with oligonucleotides complementary to single-stranded regions [16]. As a result, networks of metal nanoparticles may be constructed. At present, there are several methods for conjugation of oligonucleotides with metal nanoparticles and isolation of these particles containing a certain amount of short DNA sequences [17]. At the initial stage of constructing metal networks, the DNA network should be formed or metal nanoparticles linked to only one DNA molecules should be isolated. If several DNA molecules are attached or the DNA surface is not preformed, such a metal nanoparticle turns into a spatial cluster and the efficient assembly of the network does not occur. With the use of this method, grids with 6-μm pores for structural studies have been designed at Duke University. The DNA assembly makes it possible to place a discrete amount of nanoparticles in two-dimensional or three-dimensional space with a precision of a nanometer. A similar system may be used for the growth of nanowires [18]. The use of DNA adaptors ensures control over the assembly of multicomponent metal nanoparticles as well [19]. The variety of uses of the surface of DNA for the precise positioning of proteins, nanoparticles of transition metals, and other functional components in specially developed motifs was considered in [20].

The targeted arrangement of molecules on the surface improves the selectivity of chemical reactions. As was revealed by atomic force microscopy [21], chemical reactions with single molecules may occur in a certain DNA support-directed place. High yields and selectivity of successive cleavage and formation of bonds in these experiments demonstrated the possibility of chemical modification after the assembly of DNA nanostructures and their potential use as a locally addressed solid support. Specifically, chemical reactions between functional groups situated at different points on the DNA surface open a new kind of chemical synthesis. Thus, monodisperse macromolecules may be synthesized through a parallel process where selectivity is determined by the position and orientation of reacting molecules on the DNA support rather than by the common successive synthesis and the routine use of protective groups. The thickness of the DNA surface may be increased via the targeted joining of such surfaces (Fig. 4a).

An example of the transition to three-dimensional organization of the DNA material is provided by the assembly of a DNA cube [22]. In 2009, this assembly provided an idea to other researchers to create a cubic box (42 nm × 36 nm × 36 nm) with a cover that opened under certain conditions [23]. The scheme of the DNA cube assembly is shown in Fig. 4c. This cube in a box with a lid was assembled via two stages involving successive treatments with DNA ligase. This scheme was developed specially to avoid formation of the DNA surface. The size of the cube was 42 nm × 36 nm × 36 nm. The lid of the cube can be opened, depending on external conditions. These boxes offer promise as containers for drugs.

On the basis of DNA, the Möbius strip—a two-dimensional surface having only one side and one boundary—and the Borromean rings were assembled [24].

Another direction of shaping any figure involves the use of the DNA-origami method. This method,

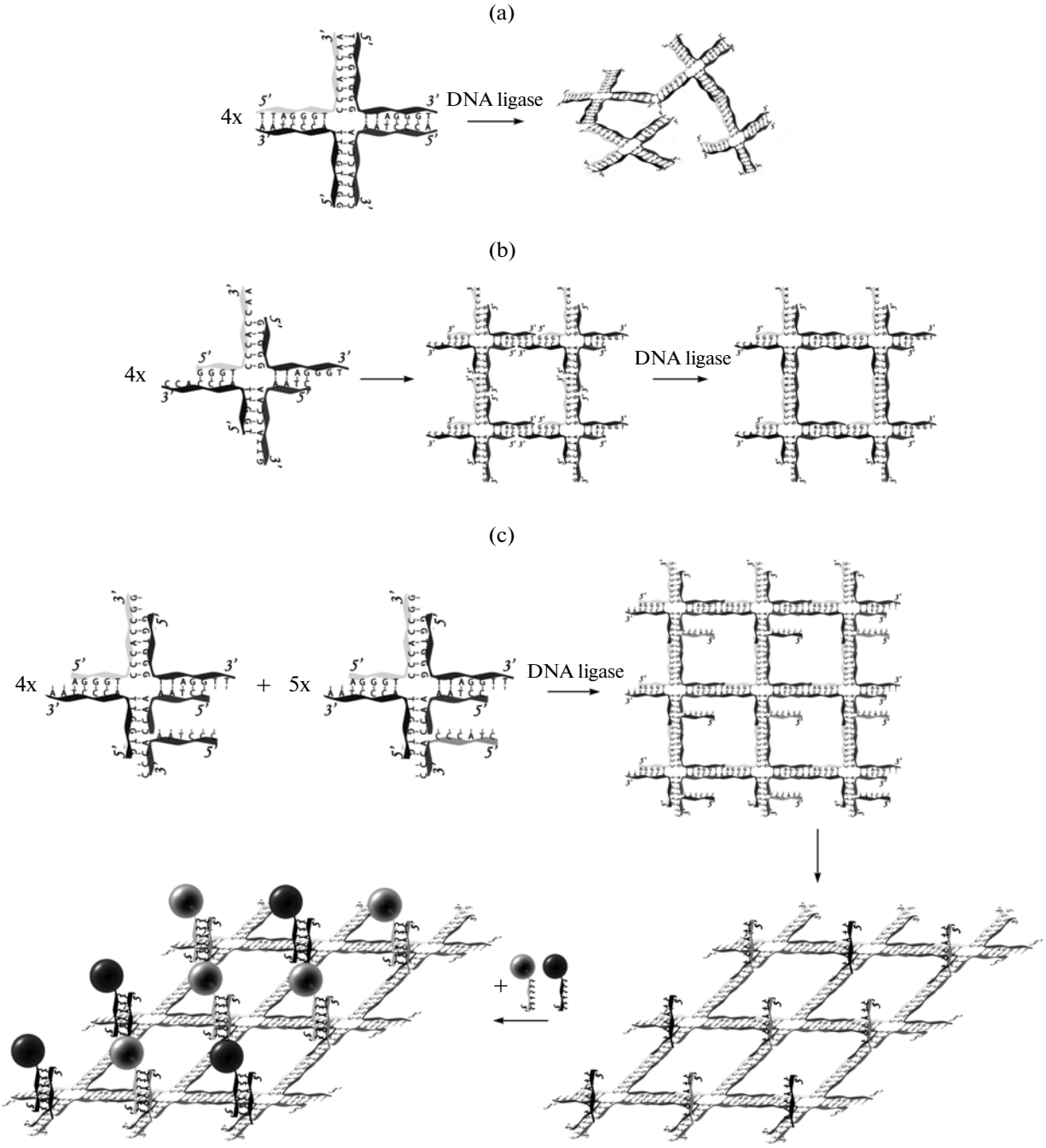

Fig. 3. (a) Scheme of the formation of the DNA from four X-shaped DNA elements, (b) scheme of the formation of the nanoscale lattice from four X-shaped elements, and (c) lattices with single-stranded regions extending over the surface and positioning of nanostructures (balls).

described by Rothmund in 2006, relies on the interaction of a long single strand of DNA with shorter DNA strands complementary to some portions of the long strand [25]. During the transition from the single-stranded region to the double helix, the coil-to-rod transition occurs (Fig. 2e). Free rotation around phosphodiester bonds of the long strand becomes hindered owing to formation of hydrogen bonds with the bases of the DNA short strand. The assembly of desired figures occurs as follows: At the first stage, the positions of double-helical and single-stranded regions are calculated. Then, the targeted synthesis of short fragments (oligonucleotides) complementary to the calculated regions is performed; finally, long and short DNA strands are mixed, and the mixture is heated to a temperature at which all randomly formed double-

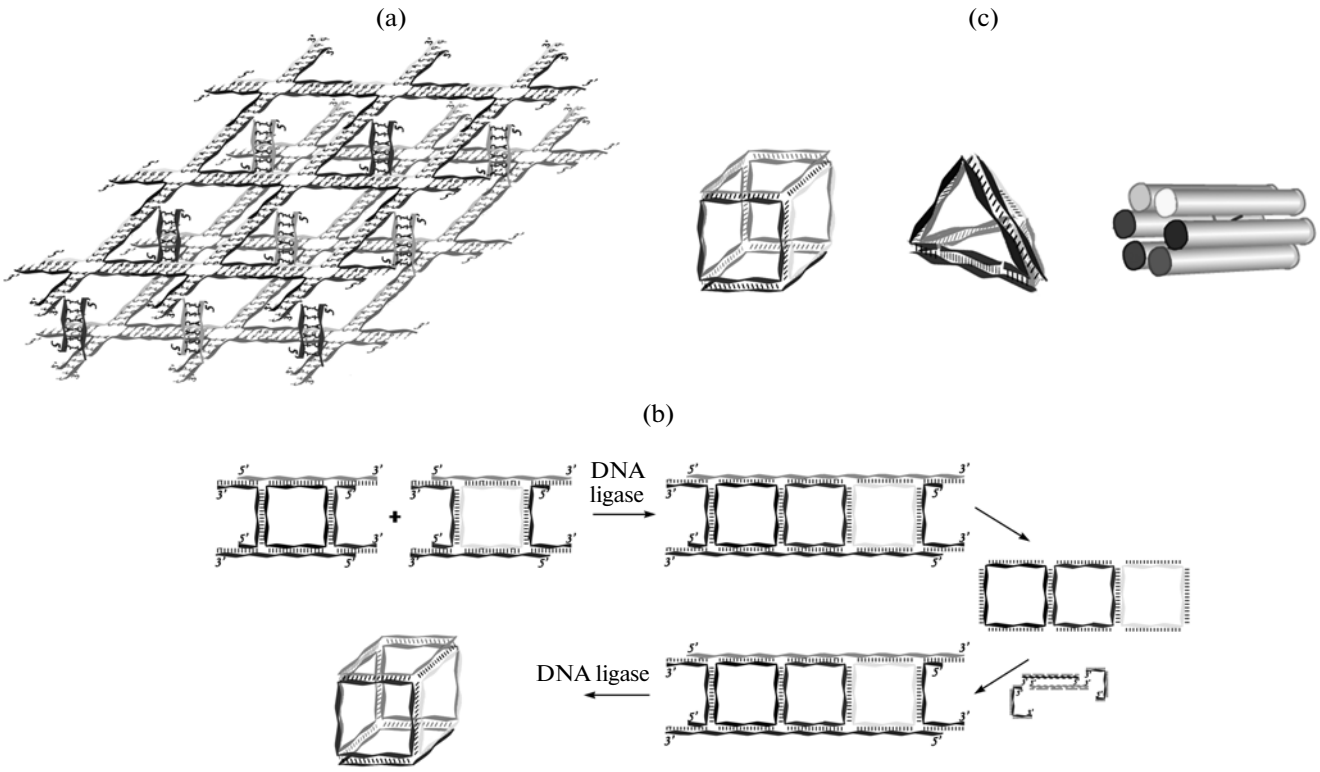

Fig. 4. Three-dimensional materials: (a) joining of two DNA surfaces, (b) various three-dimensional blocks (DNA cube, DNA pyramid, and DNA cylinder; double helices are denoted by tubes), and (c) example of DNA cube assembly.

stranded portions are unwound (Fig. 2e). During cooling, oligonucleotides occurring in excess in the mixture are joined with the predetermined portions of long strands and force them to bend as planned. The as-prepared shapes may be conditionally referred to as two-dimensional, because the width of the resulting pattern corresponds to the double-helix width. For the most widespread form, the B form, this value is 2.2 nm. Soon after the creation of two-dimensional structures, the DNA-origami technique led a transition to the three-dimensional technique. In the three-dimensional DNA-origami technique, various folded nanostructures may be assembled. These can be nanogears, nanobushings, etc. [26]. There are special programs that allow calculation of the sequences that should be synthesized to assemble the necessary structures, as described in [27]. Thus, the cylinder shown in Fig. 4c was calculated with the use of this program. Hollow tubes (from 0.1 to 1 μm in diameter) composed of 3 or 4, 6, and 20 helices may be constructed (Fig. 4b) [28]. Such nanotubes may serve as a basis for the spatial arrangement of metal nanoparticles, as exemplified by experiments in which gold nanoparticles were used to make the self-assembly process visible. [29].

There are two general approaches to using DNA origami for fabrication of engineering materials [30]. According to one approach, the assembled DNA-origami structures are utilized as templates for another material, while in the other approach, the engineering material is assembled simultaneously with the DNA-origami assembly. Thus, the DNA-origami technique is used to place molecules different from DNA in a certain position in space, thereby determining new properties of the materials. The fabrication of complex structures [30] based on the streptavidin–biotin system is evidence for the high potential of the latter approach because it may be useful for the assembly of composites with the same spatial positioning of various components.

Special attention should be given to the use of DNA materials for the construction of nanosize machines. Substantial progress has been achieved in the creation of DNA machines that have mechanical functions—such as rupturing a material or rolling—or a directed action. At first glance, the development of such systems is associated with satisfaction of purely scientific curiosity; however, extremely promising applications of such systems in the future may be highlighted. They may be applied for the manufacture of supersensitive sensors, for example, for heavy metals [31]. The combination of DNA sequences carrying catalytic function (DNAzymes) and classical DNA replication form the basis for analytical processes that could replace the protocol of the polymerase chain reaction.

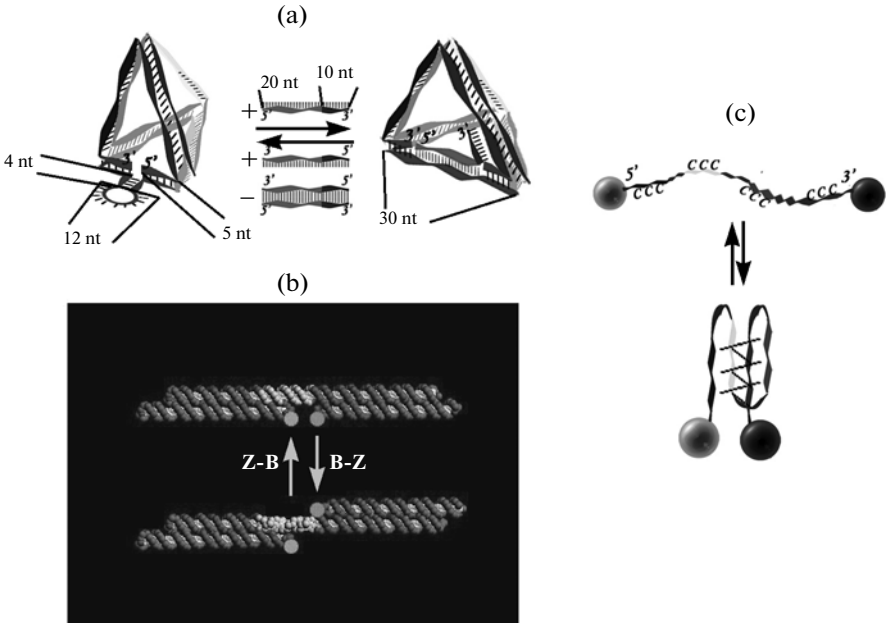

Fig. 5. Movement examples: (a) movement due to lengthening of the pyramid edge (nt is nucleotide), (b) transition between B and Z forms (reprinted with the kind permission of Nadrian C. Seeman [41]), and (c) ionic DNA switch (the fluorophore and quencher are denoted by balls).

DNA machines are valuable not only for DNA analysis but also for other analytical processes. The attachment of DNA machines as labels to antibodies and their use as immunological amplicons have provided the development of detection methods [32]. Thus, the word *machine* implies movement. How is this movement produced in DNA-based systems? The most obvious case is provided by the system referred to as "fingers" [33]. Movement is based on lengthening of one of the edges of the DNA pyramid (Fig. 5a). Let us consider the case when there is a break of the internucleotide bond in this edge of the double helix and when a chain without breaks contains a DNA hairpin (a structure in which mutually complementary regions are separated at minimum by four monomer units of the polymer and belong to the same DNA molecule). Then, addition of an oligonucleotide fully complementary to the hairpin sequence leads to its opening because the new double helix formed between the oligonucleotide and the hairpin sequences has a large amount of Watson–Crick pairs, an energetically favorable circumstance. As a result of this opening, the edge of the DNA pyramid lengthens from 22 to 30 nm [33]. This movement is reversible if the added oligonucleotide additionally contains a free portion consisting of 10 nucleotides. Addition of another oligonucleotide fully complementary to this portion returned the system to the initial position (Fig. 5a). However, the first way of effecting targeted movement was a structural change due to the transition between the B and Z forms of DNA [34]. Z-DNA forms when the sequence is comprised of poly d(GC) under low-salt conditions. A change from B-DNA to Z-DNA, that is, the transition from the right-handed helix to the left-handed one, is approximately ~128° for each G–C pair (Fig. 5b). The transition of DNA to noncanonical conformations in response to an external stimulus is a more common form of targeted movement. This system has been called I-Switch [35]. Operation of this system is schematically represented in Fig. 5c. For example, the DNA sequence contains at its ends a quencher, a fluorophore, and cytidine-rich sequences that form the noncanonical structure under certain conditions. As a consequence, the quencher and fluorophore come closer, and fluorescence changes. On the basis of this system, the first pH sensor functioning in a living cell was designed [35]. Movement may be implemented also on the basis of DNA-chain cleavage when DNAzymes are used. A system sensitive to UV light has been recently developed [36]. In addition, continuous rotation of DNA around its own sugar phosphate backbone may be attained with the aid of a simple nanomotor that is electric-field driven. The motor is composed of a DNA-assembled rotor and partially single-stranded DNAs connecting the surface and a magnetic bead. Rotation is induced by rearrangement of DNA caused by oscillation of the electric field [37].

Special attention should be paid to DNA self-assembly and lithography processes. In this case, DNA origami serves as a basis for lithography or is used in combination with surfaces for sizing. The press release from IBM dated August 2009 [38] states that

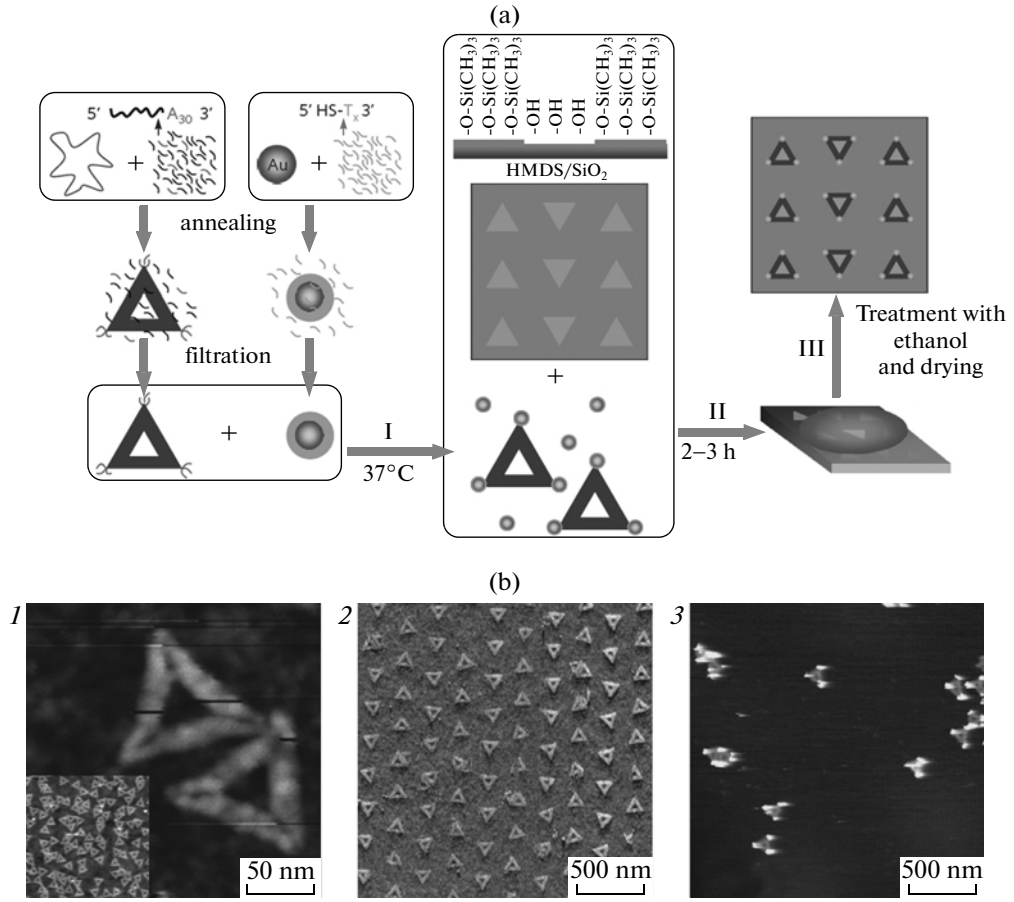

Fig. 6. The use of DNA origami and the surface sieve. (a) Scheme of assembly of the DNA triangle with gold nanoparticles in vertices, attachment of such triangles to the surface, and their purification. (b) Atomic force microscopy: (*1*) unsorted assembled DNA triangles, (*2*) triangles attached to the surface, (*3*) isolated DNA triangles with gold nanoparticles in vertices (reprinted with permission from Macmillan Publishers Ltd., Nature Nanotechnol., [39] 2009).

the combination of DNA origami and classical lithography as a method for manufacturing chips makes it possible to increase their resolution from 25 to 6 nm. DNA origami may be used jointly with the surface for sizing of nanostructures [39]. A successful scheme of this process is shown in Fig. 6a. At the first stage, DNA triangles were assembled in accordance with the DNA-origami principle, while, gold nanoparticles were modified with oligonucleotides at the same time triangles with gold nanoparticles in vertices were assembled (Fig. 6b). Sizing on the surface allowed a regular arrangement of triangles. The feasible advancement and application of this process were discussed in [40]. The final aim was to increase resolution and to control costs in the development of alternative microtechnologies.

Thus, the use of precisely DNA as the basis for creation of new materials has high developmental potential, especially in microelectronics and tissue engineering. The most plausible application is the design of materials for biomedicine: targeted release of drug components or regulator oligonucleotides and three-dimensional cultivation of cells for creation of tissues. Studies devoted to modeling of nanostructures and facilitation of their movement are now most probably cognitive in character; however, the highly efficient assembly of nanostructures will inevitably lead to their future use for the manufacture of nanorobots and will pose a problem related to the search for such structures in living cells.

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