DNA-Based Materials as Chemical Reactors for Synthesis of Metal Nanoparticles

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Abstract In this mini-review we highlight a recent progress in preparation of DNA-based matrices that can be used as reactors for templating of inorganic nanomaterials and, in particular, highlight catalytic applications of such hybrid materials. We also discuss advantages and disadvantages of DNA utilization as a material and outline prospects of DNA-based technologies in future.

1. Utilization of DNA as a sustainable material

Although ubiquitous in earth, density of DNA in a living matter can largely vary and, importantly, DNA is usually found as a complex mixture with proteins that makes isolation of pure DNA a difficult task. However, in present, DNA extracted from salmon milt by enzymatic degradation of DNA complex with proteins and ethanol extraction, is utilized commercially as a material and can be supplied in ton quantities[1] (**Figure 1**). DNA obtained by this method is still rather expensive (*ca.* $20/g), but this cost might become reasonable in applications dealing with expensive noble and rare-earth metals such as precious metals extraction, recycling, separation as well as in catalysis and nanoelectronics.

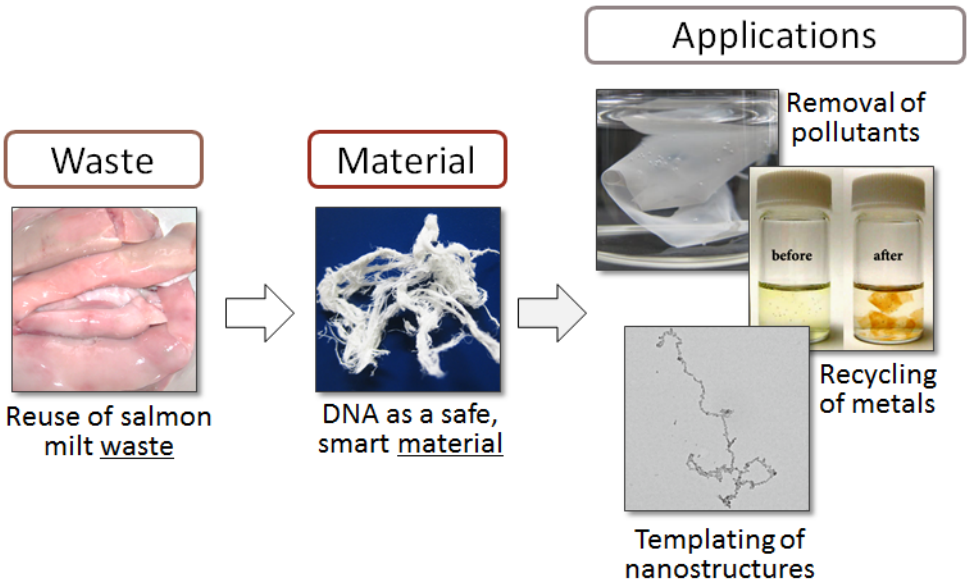

Figure 1. Application of DNA as a material. Extraction of DNA from waste salmon milt is used to obtain large quantities of DNA that are further used for materials science and environmental applications.

During the past decade, the application of natural DNA materials has dramatically broadened (**Figure 1**). DNA-based materials were applied for removal of organic and inorganic pollutants[2-4], production of inorganic nanomaterials,[5] preparation of antibacterial agent[6], construction of humidity censors[7], electrical,[8] and optical[9] materials. In the present review, we focus on an emerging application of natural DNA for templating inorganic nanomaterials (**Figure 1**).

2. Why DNA is a good template for fabrication of inorganic nanostructures?

First attempts to utilize DNA as a material for nanotechnology date back to late 90th.[10-11] Since then DNA was used for preparation of biomatrices[12-14] as well as for templating of a broad spectrum of inorganic nanostructures from individual nanoparticles to nanowires and more complex 2- and 3-dimensional architectures.[15] DNA is broadly utilized for construction of metal nanostructures because of its three important properties: (i) high affinity to most of transition metal ions, (ii) rigidity of double stranded DNA polymeric chain, and (iii) a variety of means DNA can be self-assembled and self-organized.

The former property regarding noble metal ions such as Au^{3+}, Ag^{+}. etc. is well known for several decades[16-17]. During past years DNA was found to be also efficient adsorbent for rare-earth metal ions.[18] High affinity of DNA to metal ions is important for concentrating of metal ion precursors along DNA macromolecules to be next used for metallization, i.e. formation of an inorganic phase on DNA template. DNA is negatively-charged polyelectrolyte, therefore, it interacts with virtually all metal cations and cationic complexes, but forms high-stability complexes only with those ions that coordinate with DNA bases, i.e. with transition metals ion (**Table 1**)[17].

Table 1. DNA binding sites for various metal ions.[17]

Binding site(s)	**Metal ions**
Phosphates	Li^{+}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cr^{3+}, Fe^{3+}, etc.
Phosphates + bases	Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Au^{3+}, etc.
Bases only	Ag^{+}, Hg^{2+}, etc.

Secondly, rigidity of double-stranded DNA of *ca.* 2 nm diameter having persistence length of *ca.* 50 nm (physiological salt concentration) is significantly larger than that of most of natural and artificial polyelectrolytes that are able to coordinate with metal ion precursors. Rigidity of DNA double helix is important as it provides DNA-templated nanostructures with a high mechanical stability that facilitates manipulation with DNA macromolecules. In addition, due to large volume of DNA coil intramolecular DNA-DNA contacts are seldom resulting in a high stability of metallized DNA against self-aggregation (collapse). Metallization of bulk polymeric materials is a well-known technique,[19] but the number of reports describing templating of metal nanostructures by non-DNA single macromolecules is fewer.[20-22] On the other hand, block-copolymers and dendrimers that may be considered as single macromolecule in solution were also widely used for this purpose.[23-25]

Finally, there are different possibilities for DNA self-recognition and self-assembly into programmed ordered two-[26-27] and three-dimensional[28] (2D and 3D) architectures that opens

numerous opportunities to guide the formation and growth of metal nanostructures of significantly higher structural complexity.

3. DNA-templated one-dimensional (1D) nanowires and NP arrays: limits of their use

Pioneering report of Braun et al.[29] on DNA metallization by silver nanoparticles to produce a conducting silver nanowire followed by a vast number of papers on DNA utilization as a polymeric template for preparation of one-dimensional (1D) nanostructures with a morphology of nanowires or nanoparticle arrays either grown on or assembled on DNA scaffolds[30-31] with a particular motivations to apply such structures to nanoelectronics.[32] Nearly all of metals precursors forming coordination complexes with DNA bases such as Au, Ag, Cu, Pt, Pd, etc. (**Table 1**) were tested in this regard and corresponding DNA-templated 1D nanostructures were successfully prepared[32]. Later, morphological diversity of DNA templates was extended toward 2-[27] and 3-dimensional[33] self-assembled structures, which were also successfully decorated by metal nanoparticles[34] via programmed co-assembly of scaffold DNAs and metal NP modified with DNA fragments. **Figure 2** shows representative electron microscopy images of 1D nanowires[35] and 1D arrays[36] of metal NPs templated by DNA single chain. Such DNA nanostructures are considered as promising candidates not only for electronic applications but also in catalytic, optical and sensory fields. Most of the synthetic procedures for preparation of 1D inorganic nanostructures by reduction of DNA-bound metal precursor are relatively simple and well established, but applications of these materials are limited mainly due to an ease of their aggregation in solutions: high surface energy of nanometer size metal structures attached to DNA inevitably causes “stickiness” of NP and formation of nanowires aggregates that cannot be reversibly dispersed into aqueous solutions. This issue can be resolved in part by attaching DNA to a suitable solid template before or after metal phase growth. For example, 2D metal nanowires were produced by attaching λ-DNA molecules onto glass substrate into parallel or crossed patterns followed by subsequent metallization[37] (**Figure 2c**) In another example, 2D DNA-templated nanostructures bound to micrometer size bead were obtained using two-step “double-templating” approach: electrostatic binding of anionic DNA to cationic microsphere followed by standard DNA metallization protocol[38-39] (**Figure 2d**). The above methods suffer from disadvantages such as low stability of DNA-templated networks of inorganic materials and consequent difficulties to obtain stable stand-alone nanostructures after removal of the supporting substrate.

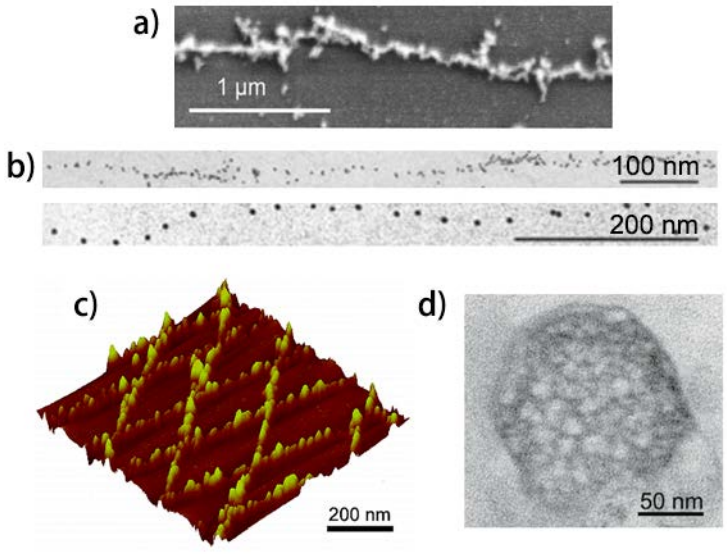

Figure 2. One and two-dimensional DNA nanostructures. (a) DNA strand continuously coated with a Pd[35] (Reprinted with permission from Richter, J.; Mertig, M.; Pompe, W.; Monch, I.; Schackert, H. K., Appl Phys Lett 2001, 78 (4), 536-538. Copyright AIP Publishing). (b) One-dimensional arrays of gold nanoparticles on a long DNA chain with repeating oligonucleotide sequences hybridized with oligonucleotide-modified gold nanoparticles[36] (Reprinted with permission from Deng, Z. X.; Tian, Y.; Lee, S. H.; Ribbe, A. E.; Mao, C. D., Angew. Chem. Int. Edit. 2005, 44 (23), 3582-3585. Copyright John Wiley and Sons). (c) Two-dimensional pattern of DNA nanowires deposited on a flat surface[37] (Reprinted with permission from Deng, Z. X.; Mao, C. D., Nano Lett 2003, 3 (11), 1545-1548. Copyright 2003 American Chemical Society). (d) Network of DNA mineralized by CdS on a solid micrometer spherical template of SiO_2 bead[39] (Reprinted with permission from Pu, S. Y.; Zinchenko, A. A.; Murata, S., Langmuir 2011, 27 (8), 5009-5013. Copyright 2003 American Chemical Society).

In view of the above, construction of continuous 2- or 3-dimentional DNA matrices is still required to provide a DNA-based hybrid material with an enhanced stability. In this regard, next we describe new studies on DNA multilayers and DNA hydrogels that can be utilized as working 2- and 3-dimentional DNA templates, respectively, and show their applications as reactors to generate inorganic nanomaterials.

4. Three-dimensional matrices: DNA hydrogels

Three dimensional DNA matrices are represented by DNA hydrogels, a new type functional materials[40-41]. There have been a number of techniques developed to synthesize DNA hydrogels. One part of them takes advantage of complementary recognition and bridging of DNA strands by enzymatic ligation,[42] hybridization of short complementary DNA fragments[43-44], etc. Despite effective structural control gained in such DNA hydrogel systems[45] preparation of DNA fragments with a certain nucleotide sequences necessary for complementary recognition is complex and biologically-relevant media is usually required for DNA biochemical reactions to crosslink DNA. On the other hand, a more facile synthetic method is based on a straightforward chemical cross-linking of random sequence natural DNAs such as those extracted from a fish milt (**Figure 1)**. DNA cross-linking by ethylene glycol diglycidyl ether (EGDE) (**Figure 3**) was first reported by Tanaka et al.[46] and later was utilized by a number of research groups[40, 47-48]. Usually, such DNA hydrogels contain 1-5% of DNA and are characterized by low dsDNA contents due to substantial denaturation of DNA necessary for cross-linking reaction to occur. Alternatively, DNA can be incorporated into hydrogels of other synthetic polymer matrix either by chemical bonding[6, 49] of through formation of physical hydrogel from DNA upon melting[50-51].

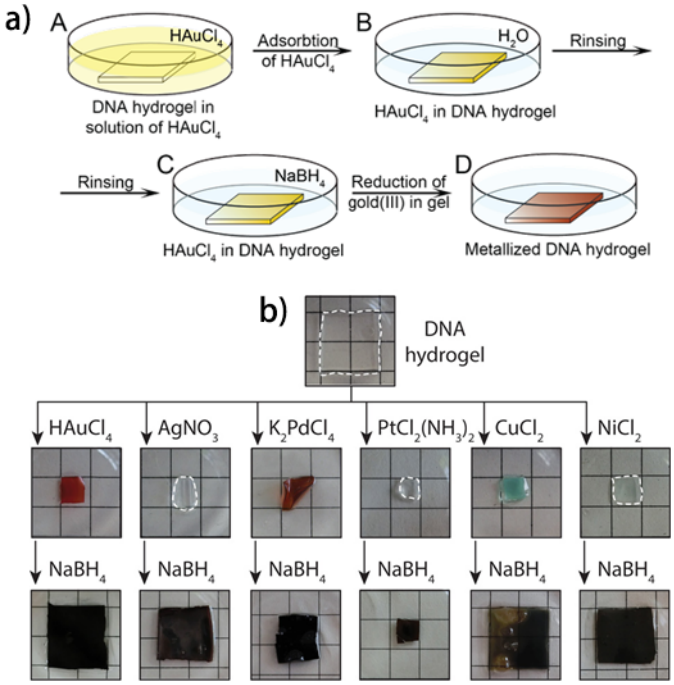

Figure 3. (a) Schematics of DNA hydrogel metallization by absorption of $HAuCl_4$ by DNA hydrogel, rinsing of DNA hydrogel by water, addition of the reduction agent to DNA hydrogel, and reduction of Au ions[52]. (Reprinted with permission from Zinchenko, A.; Miwa, Y.; Lopatina, L. I.; Sergeyev, V. G.; Murata, S., ACS Applied Materials & Interfaces 2014, 6 (5), 3226-32. Copyright 2014 American Chemical Society) (b) Photographic images of DNA hydrogel films before and after binding of Au, Ag, Pd, Pt, Cu, and Ni metal precursors, respectively, and metallization by reducing metal ions with $NaBH_4$[53]. Grid size is 6 mm. (Reprinted with permission from Zinchenko, A.; Che, Y. X.; Taniguchi, S.; Lopatina, L. I.; Sergeyev, V. G.; Murata, S., J. Nanopart. Res. 2016, 18 (7), Copyright Springer Publishing Company)

5. Two-dimensional matrices: DNA-based multilayers

In contrast to single layer of metallized DNA described above (**Figure 2c,d**), considerably more stable polymeric films are formed by increasing a number of layers. Multilayers containing DNA can be prepared by well-established layer-by-layer (LbL) deposition approach using oppositely charged polyelectrolytes, one of which is DNA[54-56] (**Figure 4a**).

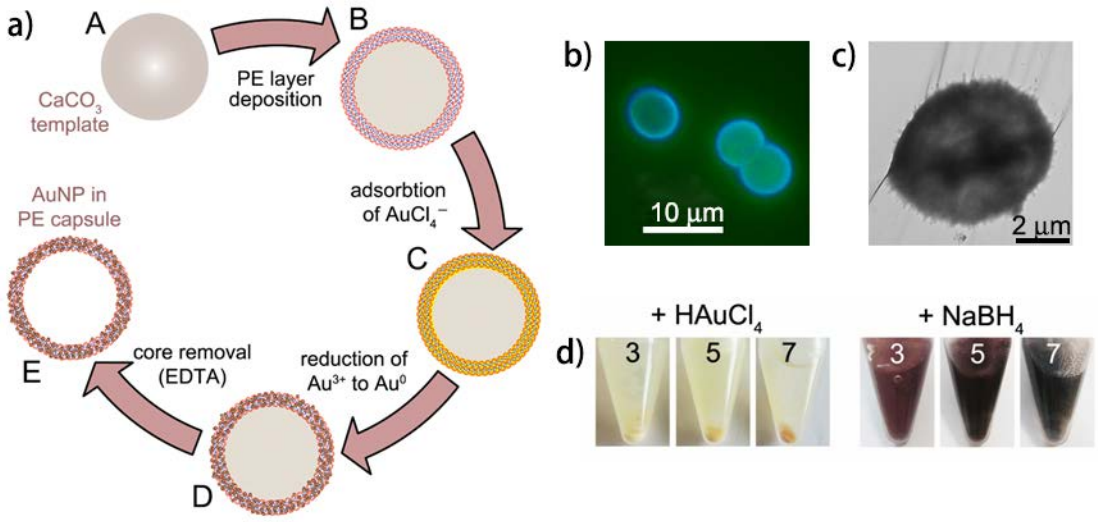

Figure 4. (a) General schematics illustrating the construction of polyelectrolyte multilayers and their metallization. (b) Typical fluorescent microscopy images of $CaCO_3$ beads with deposited polyelectrolyte multilayer stained by DNA-specific DAPI fluorescent probe (blue) and by Ca^{2+} specific calcein florescent probe (green). (c) TEM images of a typical 5-layers capsule. (d) Photographic images of $CaCO_3$ beads containing 3, 5, and 7 polyelectrolyte layers after saturation

with $HAuCl_4$ (left), and sequential reduction by $NaBH_4$ (right). (Adapted with permission from Zinchenko, A.; Nagahama, C.; Murata, S., ChemNanoMat 2016, 2 (2), 125-132. Copyright John Wiley and Sons)

DNA and oppositely charged polycation, for example, such as poly(diallyldimethylammonium chloride), interact electrostatically forming inter-polyelectrolyte complexes (IPEC) of a high stability (**Figure 4a-c**). In thus formed multilayers, DNA preserves its role of metal ion efficient adsorbent, therefore, the multilayers can be easily saturated with a transition metal ion by dipping of multilayers into solution of corresponding metal ion precursor (**Figure 4d(left)**). Micrometer size sacrificial inorganic templates, $CaCO_3$ beads, can be finally removed to obtain stand-alone IPEC films of capsular morphology (**Figure 4c**).[56] Due to the rigidity of dsDNA molecules the resulted multilayers gain extra stability in comparison to other flexible polyelectrolytes and even capsules containing a small number of layers retain their spherical shape upon removal of $CaCO_3$ template, withstand high osmotic pressures and extreme pHs. It should be noted that most of hitherto published articles on DNA-based multilayers referred either to localized gene delivery systems enable controlled DNA release[57-58] or to DNA-CNT sensors[59-60] as a primary research goals, while there are only a few reports on metallization protocols.[56]

Considerably thicker water-insoluble DNA thin films were obtained by DNA complexation with surfactants,[8, 61] or ionic liquids[62], or by photochemical DNA crosslinking under UV irradiation.[63] However, the intrinsic water insolubility and consequent poor diffusion of chemicals inside such films limit their application as chemical reactors.

6. Synthesis of metal nanoparticles in DNA matrices

Metal nanoparticles in DNA-based matrices are generally prepared by protocols illustrated in **Figures 3a and 4a** for hydrogels and multilayers, respectively. First, metal ion precursor binds to DNA and then it is chemically reduced resulted in a formation of metal nanoparticles embedded into DNA-based matrix.[52] Absorption amount of transition metal ions is typically 0.3-0.8 ion (or ion complex) per DNA monomer unit (nucleotide) and may require up to several hours for equilibrium to be reached.[53] Binding of metal ion is usually accompanied by DNA hydrogel shrinking due to partial neutralization of DNA negative charges (**Figure 3b**) by cationic metal species. Subsequent reduction of metal ion precursor by a suitable reducing agent leads to

formation of neutral metal atoms and growth of metal nanoparticles (NP). Analysis of TEM images of metal nanoparticles after dispersion of hybrid hydrogel by ultrasonication or enzymatic degradation (**Figure 5a**) indicates that the size of metal nanoparticles grown in DNA-matrices is very small, 2-3 nm in average, with a little variation between metals. Size of nanoparticles can be tuned to some extent by changing the speed of metal ion reduction. For example, fast reduction of gold complex in alkali media produces 2 nm size NP, while slow reduction at pH 4 results in a formation larger gold colloids of *ca.* 10 nm average size[64].

By comparing the size of gold nanoparticles obtained in DNA hydrogel and other synthetic hydrogels[65-68], it was noticed that generally DNA templated nanoparticles are smaller which may be related to a facile nucleation of metal clusters on a DNA template. Nanoparticles formed in DNA matrix do not affect significantly the properties of the matrix: hybrid DNA hydrogel containing gold NPs showed typical shrinking/swelling polyelectrolyte behavior by changing of an ionic strength of a solution (**Figure 5b**)[64]. Nanoparticles are firmly bound to DNA matrix, therefore, they do not diffuse off the hydrogel matrix and no lateral diffusion inside the hydrogel happens (**Figure 5c**).

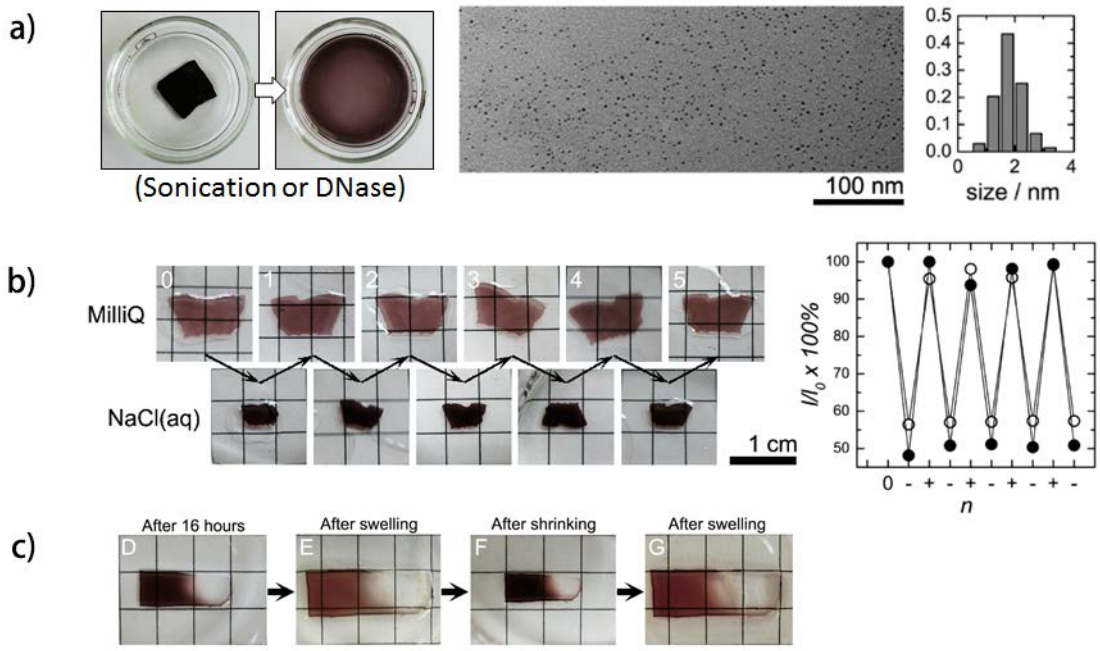

Figure 5. (a) Photographic images of metallized DNA hydrogel before after dispersion into aqueous solution, TEM images of gold nanoparticles obtained by DNA hydrogel dispersion and typical distribution of their sizes (Adapted with permission from Che, Y.; Zinchenko, A.; Murata,

S., Journal of Colloid and Interface Science 2015, 445, 364-70, Copyright Elsevier). (b) Photographic images of Au-metallized DNA hydrogel sequentially transferred to distilled water (MilliQ) and 100 mM NaCl solutions and corresponding dependences of the hydrogel linear size change obtained for 100 mM NaCl solution (open circles) and 200 mM NaCl solution (filled circles)[64] (Adapted with permission from Miwa, Y.; Zinchenko, A.; Lopatina, L. I.; Sergeyev, V. G.; Murata, S., Polym. Int. 2014, 63 (9), 1566-1571, Copyright John Wiley and Sons). (c) Photographic images of partly metallized DNA hydrogel by Au (the colored part is metallized) after successful placing in water and saline solutions.

Recently, DNA hydrogel was also successfully applied to template multi-element nanoparticles[69], which preparation in aqueous solution is particularly challenging. By extending DNA metallization protocol for preparation of matrix-embedded NP to three or four steps of successive saturation of DNA matrix with each metal precursor and reduction (**Figure 6a**), this approach can be practically used to obtain either alloy or core-shell type of bimetallic colloids of a few nm size[69] (**Figure 6b**). In principle, this method allows preparation of a broad variety of bimetallic and even trimetallic metal colloids.

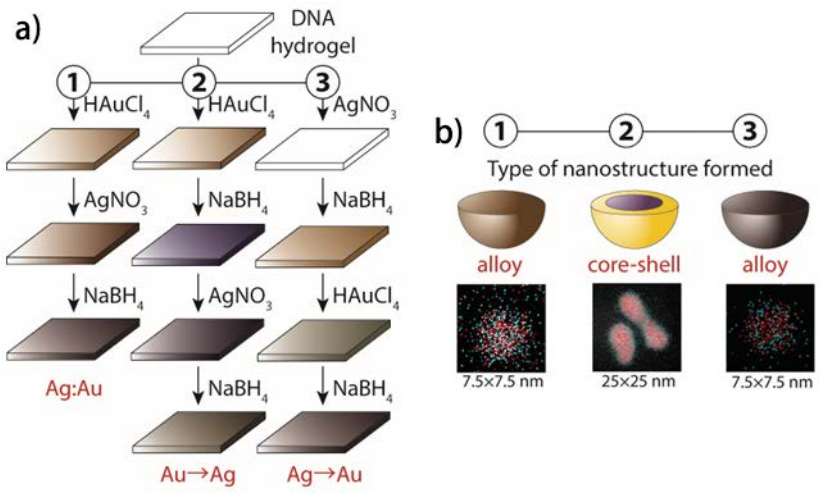

Figure 6. (a) Schematic outline of three routes to prepare Ag-Au bimetallic nanostructures inside DNA hydrogels[69]. (b) Type of bimetallic NP formed inside DNA hydrogels according to three routes shown in (a) and corresponding element mapping (HAADF-STEM) of Ag (red) and Au (blue) elements in the obtained NPs. (Adapted with permission from Taniguchi, S.; Zinchenko, A.; Murata, S., Chem. Lett. 2016, 45 (6), 610-612, Copyright the Chemical Society of Japan)

Similarly to DNA hydrogels, DNA-based multilayers can be also used as “reactors” for metal nanoparticles preparation (**Figure 4a**). Saturation of DNA-containing polyelectrolyte multilayers and reduction of a complexed metal ion (complex) inside the multilayers generates ultrafine nanoparticles distributed evenly and without aggregation inside the multilayer matrix (**Figure 7**)[56].

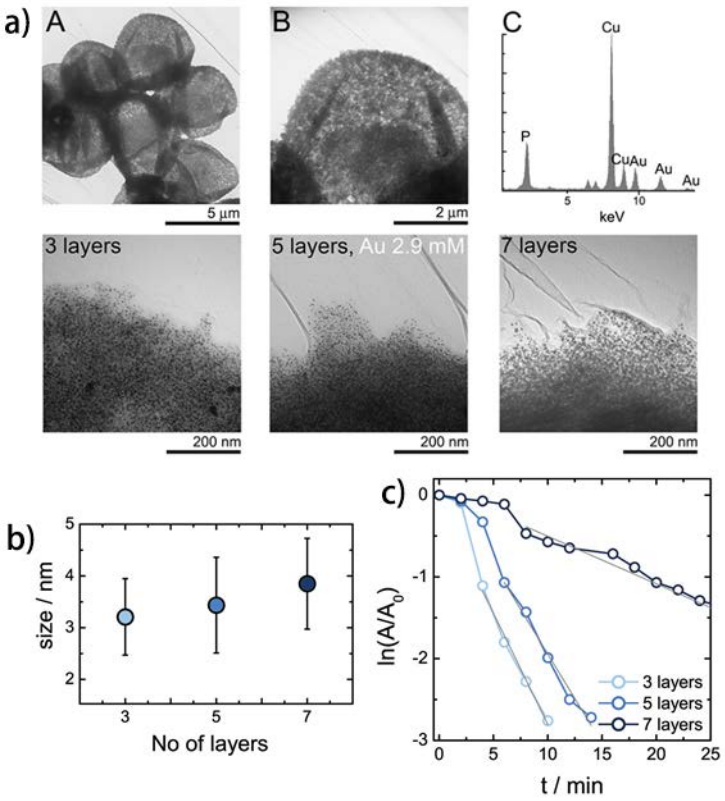

Figure 7. (a) TEM images of the typical 5-layers capsules after metallization with gold, EDS spectra of the capsule, and magnified TEM images of metallized multilayers containing 3, 5, and 7 polyelectrolyte layers, respectively[56]. (b) Dependence of the average size of gold nanoparticles synthesized in multilayers on the number of layers in a capsule. (c) Time dependence of the normalized nitrophenol absorbance at λ= 400 nm in solutions containing multilayered capsules with 3, 5, and 7 polyelectrolyte layers. (Adapted with permission from Zinchenko, A.; Nagahama, C.; Murata, S., ChemNanoMat 2016, 2 (2), 125-132. Copyright John Wiley and Sons)

Free-standing capsules with embedded NP can be obtained by a dissolution of $CaCO_3$ core by either hydrochloric acid or EDTA. In contrast to DNA hydrogels, DNA multilayer films possess

higher mechanical stability and a resistance to biodegradation: neither sonication nor enzymatic treatment induce film disintegration or redispersion of matrix-bound NP into solution. The size and dispersion of NP in DNA-based multilayers shows little dependence on the number of layers in multilayered films (**Figure 7b**).

Earlier, a number of reports described preparation of metal nanoparticles in multilayered capsules constructed from synthetic polyelectrolytes[70-74]. Importantly, most of multilayered films constructed from synthetic polyelectrolytes produce nanoparticles larger than 10 nm, while the average size of NP prepared in DNA-based capsules is very small and similar to size of NP prepared in DNA hydrogels, i.e. 2-3 nm (**Figure 7a**).

It should be noted that usually synthesis of unprotected metal nanoparticles in water results in their aggregation, synthesis of metal NP in concentrated solutions of DNA produces similar size metal NP to those prepared in hydrogel with somewhat broader size distribution. However, utilization of DNA matrix such as DNA hydrogel or DNA multilayered film is more practical because being incorporated into matrix of permeable hydrogel NP can be easily separated from solution, purified, stored, and manipulated by a number of transfer steps to a suitable solvent or solution. Overall, the merit to use DNA as a component of multilayered reactors is two-fold: (i) synthesis of smaller nanoparticles with broader mass-to-surface area, and (ii) universality of DNA binding to most of transition metal ions which is valuable for construction of multicomponent systems.

7. Catalytic activity of metal nanoparticles embedded in DNA matrices

Catalysis by metal NP is of outstanding importance and it has been vigorously studied for past several decades[75-76]. Small size of NP is one of key factors that control efficiency of catalysis due to a large surface area gain. However, dispersions of small metal nanocolloids are usually unstable and easily aggregate, thus stabilization of NP as well as their separation and dispersion issues inevitably arise and narrow applications of NP colloids as catalysts. Incorporation of catalytic NP into a polymeric matrix allows for stabilization of metal NP and such hybrid materials attracted considerable attention and has been intensively studied during recent years[77]. DNA is particularly suitable as a matrix because DNA can play a role of active component taking part in binding to metal precursors, size-controlled formation of NP and their stabilization.

Nanoparticles of various transition metals synthesized in DNA hydrogels (**Figure 3b**) demonstrate a certain catalytic activity as was confirmed using a model reaction of *p*-nitrophenol reduction to *p*-aminophenol in aqueous solutions[53] (**Figure 8**). Either metallized hydrogel or metallized multilayered capsules are added to a reaction mixture where catalytic reduction is performed. Catalysis of nitrophenol reduction by NP of various metals in each type of DNA matrix obeys the pseudo-first-order reduction kinetics (**Figure 8b**). Although certain amount of DNA is supposed to be attached to metal NP surface, until now there were no experimental evidences demonstrating the effect of DNA on NP catalytic properties. The correlation between catalytic activities of NP of various metals in DNA hydrogels roughly corresponds to the correlation between catalytic activities of corresponding NP dispersions[53].

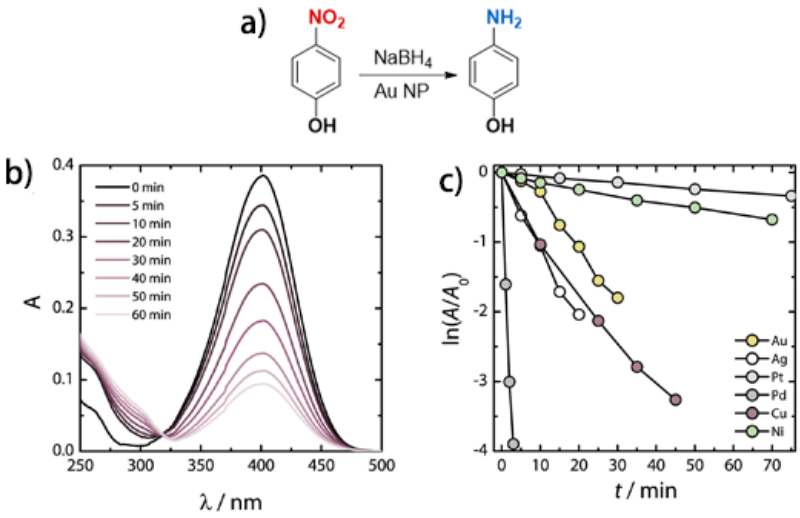

Figure 8. (a) Reaction of *p*-nitrophenol reduction by $NaBH_4$ using gold NP as catalyst. (b) Time-dependent changes in UV-vis absorbance spectra of *p*-nitrophenol with containing $NaBH_4$ reducing agent and DNA hydrogel metallized by silver. (c) Kinetic curves of *p*-nitrophenol reduction catalysed by hybrid hydrogels containing NP of various metals built in coordinates of the first-order kinetics. The slope of kinetic curve obtained for *p*-nitrophenol redaction without catalyst was zero. (Adopted with permission from Zinchenko, A.; Che, Y. X.; Taniguchi, S.; Lopatina, L. I.; Sergeyev, V. G.; Murata, S., J. Nanopart. Res. 2016, 18 (7), Copyright Springer Publishing Company)

Although the direct comparison of NP catalytic properties synthesized in DNA hydrogel and in synthetic hydrogels[77] is difficult due to a large number of parameters such as NP loading degree, NP size, hydrogel density, etc., in general, DNA hydrogel is favorable candidate as a matrix due to formation of small size NP which catalytic properties are usually superior compared to larger ones[78-81]. The same is true for DNA-based multilayers. Another certain merit to use NP embedded into polymer matrix is the ease of operation of such material during catalytic process. Utilization of metal NP colloidal suspensions as catalyst requires laborious steps including separation and redispersion of ultrafine nanoparticles during catalytic process. This problem does not occur for hybrid hydrogels or multilayers, which separation is very simple and no redispersion and stabilization of NP is required.

On the other hand, there is a number of clear drawbacks to use catalytic NP embedded in a polymeric matrices. In comparison to NP dispersions, gross catalytic activity of NP in polymeric matrices is low.[82] For instance, about 40-fold decrease of reaction rate was demonstrated for NP catalysts embedded in a DNA hydrogel.[82] The fundamental reason of this decrease is a slow diffusion velocity of reactant inside polymeric materials, especially in hydrogels, where kinetics is diffusion-controlled[76]. Consequently, as only NPs in the surface layer of a hydrogel take active part in a catalytic reaction, optimization of geometry and structure of such hybrid hydrogels is essential to minimize the fraction of NP that are not accessible to reactants due to diffusion problems. In contrast to hydrogels, catalytic rates for gold NP in DNA-based multilayers are higher than in hydrogels due to a better accessibility of catalytic centers to reactants (**Figure 7c**). Interestingly, even in multilayers catalytic rates were found to decrease with an increase in the number of layers in multilayers capsules, which is also considered to be affected by retarding of reagents diffusion rates in more dense multilayers.

Polyelectrolyte properties of DNA as a component of polymeric matrix can be used as a tool to control catalytic activity of NP embedded inside the matrix[82]. For example, swelling degree of DNA hydrogel that can be easily changed by adding low molecular electrolyte such as NaCl, affects catalytic rates significantly resulting in about 10-fold increase of catalytic rates over the same hybrid hydrogel catalyst upon 5-fold swelling of a hybrid hydrogel[82]. Again, higher diffusion constants in the swollen hydrogel result in faster overall kinetic rates. Similar way to control catalytic activity of hybrid materials containing catalytic NP by external stimulus was proposed for thermosensitive synthetic polyelectrolytes such as PNIPAm: collapse transition of PNIPAm

network above low critical solution temperature (LCST) suppresses drastically the catalytic performance of NP [83-88]. The above examples show principle possibility to control catalytic performance of hybrid hydrogel by an external stimuli, and since there exist a great number of approaches applicable to polyelectrolyte matrices, development of more elaborate and functional systems is anticipated.

8. Conclusions and perspectives

Combination of high affinity of DNA to transitional metal ions, its mechanical rigidity, and polyelectrolyte nature makes DNA a unique molecule for construction of different matrices that can be used as reactors to synthesize a broad variety of hybrid nanomaterials for catalysts, adsorbents, optical devices, components of electric circuits, etc. In present, much is known about DNA molecule metallization and self-assembly of DNA-guided nanostructures of a high complexity and hierarchy; however, utilization of DNA as a template similarly to synthetic polyelectrolytes is still a very far goal. This gap can be explained in part by the nature of DNA itself. Among critical problems related to the utilization of DNA as a basic construction material, poor stability of DNA under harsh experimental conditions and biodegradability are the issues that limit DNA utilization. Therefore, development of large-scale synthetic procedures must be supplemented with their optimization taking into account intrinsic properties of DNA itself. Stability of DNA can be substantially increased by attaching DNA on a surface of a template, assembly into high-density structures, formation of complexes with polymers of surfactants, etc. Despite of above problems, many new successful trials to give DNA a new life as a construction material reported since 2000 year let us hope that during forthcoming decade a number of DNA-based materials will be commercialized and its practical applications will further broaden.

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