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On the Way of DNA Metallization: Principle, Methods, and Recent Applications

Yasin Albarqouni [a], Gomaa A. M. Ali [b], Ab. Rahim Mohd-Hairul [a], Kwok Feng Chong [a,*]

[a] Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, Gambang, 26300 Kuantan, Malaysia
[b] Chemistry Department, Faculty of Science, Al–Azhar University, Assiut, 71524, Egypt

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Abstract

Recent years have witnessed tremendous coherent growth with great achievements on the DNA metallization approach, from its simple synthesis techniques to the present construction of wide range nanostructures for versatile applications in different disciplines, including chemical catalysis, environmental, or bio-sensing, and biomedical engineering. Hence, our aim here is to provide as much as possible a coherent review, leading to illustrate the research achievements on DNA metallization since revealing the DNA metal back in 1998. A systematic and comprehensive illustration starts with DNA fundamental knowledge with a brief discussion on the outstanding chemistry enrichment that denotes DNA the capability to tune metal's growth on its helix, the next section is presenting various reported construction methods and techniques of the grown metals. Afterward, the discussion is elaborated on the applications of DNA-metal nanomaterials in different fields. For that, the present work could be considered of great value to provides promotion for future works of DNA metallization with enjoying researchers from different fields.

1. Introduction

In the recent decade, DNA is enjoying intense attention and interest not only in the molecular biological systems but also in the material world as an advanced material due to its outstanding properties [1]. Taking after Watson and crick revealed the mystery of the DNA helical structure. Such properties are the meniscal size with an Angstrom-scale resolution [2], stiffness with a persistence length of around 50 nm, conductivity,

and its ability to act as a platform due to its functional group's variety makes it a super-molecule to appeal those features in advanced nanomaterial applications [3]. The construction of nanomaterial could be achieved by two strategies; either the top-down systems, where the manipulation of the number of the atoms or the molecules in the microscopic level usually used to achieve the constructed nanomaterial or the bottom-up, where molecules are self-assembly together in a parallel step as a function of the self-recognition capability of the molecules.

The fact that DNA can practice self-assembly phenomena is due to its capability to recognize molecules and sup molecules [4], which means, DNA can construct wild and different architectures [5]. In recent years, DNA metallization [6] and DNA hydrogel templating [7] are examples of self-assembly of the DNA that aim to obtain a shape-controlled nanomaterial construction for a variety of biomedical and bioelectronics applications. For that, versatile applications and numerous methodologies had been reported after enormous efforts and works are still in the same direction to overcome the proposed methods, applications, and challenges obstacles.

1. DNA Metallization
1.1 Principle

Metallization is the process where metal nanoparticles used to intercalate or assembled in a specified manner to reach nanofabricated structure either as a pure material or as a composite one. Until recent days, the metallization process was performed by top-down methods such as microcontact printing, chemical reduction, or pyrolysis to construct a variety of nanomaterials such as nanotubes, spherical nanoparticles, and nanoclusters [8–10]. Recently, an enormous coherent effort has been made to overcome the non-

controlled shape architectures as a drawback from the top-down methods, therefore using a directing assembly template was the most convenient idea. Therefore, bottom-up nanofabrication using a biomolecular template has been intensively studied to control the nanofabrication process by a precise tune of the molecular and atomic levels in the crystalline growth structure [11,12]. DNA is among those biomolecules, which is considered as a super-molecule for directing the metal deposition process. The most used metal form is metal salts, which is employed as a precursor of the deposition, where DNA is reducing those salts and directing the nano-assembly of the construct.

The first nanostructure that had been assembled using DNA as a bio-template was the conductive silver nanowires on a bacteriophage λ-DNA counter in 1998 by Braun and his co-workers [6]. Their work inspired many scientists to try constructing other metals, including Au, Pt, Fe, Ni, and many others (Table 1). A better understanding of DNA nature allows the rapid growth of using DNA in nanomaterials applications. Recently, the ability to tune the nanostructure of the constructed templated material allows scientists to reveal the physicochemical properties of DNA (e.g., magnetic, catalytic, conductance and optical), which have a direct impact not only on fabricating the nanowire but also on achieving full applications in broadening fields ranging from catalysis to energy conversion, electronics, photonics, therapeutics, and sensing.

1.2 DNA metallization methods
2.2.1 Chemical reduction

The most abroad used method for DNA metallization is the chemical reduction of the proposed metal salts, as mentioned previously, the proposed principle was first studied by Braun with co-workers. Their proposed method starts with the

activation step, where λ-DNA is assembled between two parallel gold electrodes. λ-DNA hybridized with a complementary oligonucleotide bounded in the electrode surface that working as an anchor. The second step is a selective localization of the silver ions on the DNA counter molecule in terms of ion-exchange processes. A subsequent reduction using hydroquinone is followed, where the development of a 12 mm long, 100 nm wide conductive silver nanowire between the two gold electrodes is initiating. Despite its drawbacks, the proposed decent report promotes great success in nanowire tuning.

Table 1: Summarized work on DNA-template for metals nanowire fabrication.

| Metal ions	DNA segment	Metal ions source	Reductive species	Ref.
Silver	λ-DNA	$AgNO_3$	Hydroquinone	[6]
	λ-DNA	$AgNO_3$	Sunlight	[35]
	λ-DNA	$AgNO_3$	UV light (366 nm)	[18]
	T4 DNA	$AgNO_3$	UV light (254 nm)	[36]
	Salmon tests DNA	$AgNO_3$	UV light (260 nm)	[37]
	λ-DNA	$AgNO_3$	Aldehyde	[24]
	900-mer dsDNA	$Ag(NH_3)_2OH$	Dialdehyde	[30]
	Yeast polη gene	$Ag(NH_3)_2OH$	Galactose	[31]
	4 X 4 tile nanoribbons	$AgNO_3$	Aldehyde	[38]
Latinum	λ-DNA	$Pt(NO_3)_2$	UV light (254 nm)	[39]
	λ-DNA	K_2PtCl_4	DMAB	[40]
	Poly (GC)-(AT)	$Cis-Pt(NO_3)_2$	DMAB	[41]
Palladium	λ-DNA	K_2PdCl_4	DMAB	[42]
	λ-DNA	$(NH_4)_2PdCl_2$	UV light (260 nm)	[43]
Gold	Herring tests DNA	$HAuCl_4$	λ-DNA	[44]
	ssDNA	AuNPs	NH_2OH	[45]
	Salmon tests DNA	$HAuCl_4$	UV light (260 nm)	[21]
	M13mp18 ssDNA	$HAuCl_4$	$NaBH_4$	[17]
Copper	λ-DNA	$Cu(NO_3)_2$	Ascorbic acid	[46]
	Salmon DNA isolation	$Cu(NO_3)_2$	Cu^+ ions	[47]
Nickle	λ-DNA	$NiCl_2$	$NaBH_4$	[48]
hodium	ctDNA/λ-DNA	$RhCl_3.H_2O$	$NaBH_4$	[49]

Following the same method, Richter and co-workers demonstrated a method for Palladium (Pd) growth on DNA, in their work, they mentioned an Ohmic transport behavior due to the nanowire at room temperature [13]. Although the breakthrough of the proposed method, it still has significant drawbacks including, the irregular structure due to the fast-kinetic growth, furthermore, the lake of selectivity regarding the desired DNA strand and the undesired growth of the metal in the background. The contamination or the destruction of the DNA template due to the use of corrosive reducing agents via chemical attack [14–16].

Efforts never stopped to overcome the previously mentioned drawbacks, most recently, Woolley with co-workers, reported the synthesis of a single connected Gold-Tellurium nanowire with a highly site-specific metallization [17], they reported a chemical reduction of the $HAuCl_4$ by using $NaBH_4$ as a reducing agent. Interestingly, for the first time, they illustrate a new method to employ semiconductors as a junction of the metal nanocomposite, they used Tellurium to form Au-Te-Au composite. The findings were as a strike to many researchers, promoting them to develop new semiconductors on the DNA metal construction.

2.2.2 Photoreduction

Since using chemical reducing agents could be harmful due to toxicity to either the environment or to the bio-template, a new approach has been developed recently, where mainly reduction of the metal salts achieved by an intrinsic light wave in a process called photoreduction. A fast and clean method is first reported by Berti with co-workers; they reported the reduction of silver salts to form a nanowire chain in the presence of DNA [18]. Normally, organic ligands are used as a capping and sensitizing compounds to facilitate the metallization process [19]. In the proposed process,

DNA role was a capping legend and a sensitizing agent, DNA adsorbed the Ag^+ ions then UV light in 254 nm range employed to irradiate the compound, in this step a photoinduced deposition started along with the DNA chain, which directed the construction of the Ag^+ nanowires. The obtained nanowire characterized by AFM, as illustrated in Figure 1. Similar processes of a homogenous distribution to obtain different nanowires were reported [20–23] as summarized in (Table 1).
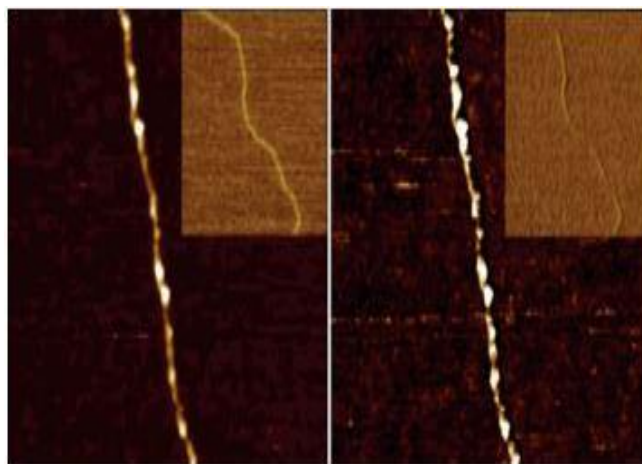
Figure 1: AFM tapping mode images of (left) height and (right) phase of a DNA-Ag^+ complex photo reduced on mica. (Adapted with permission from Ref. [18], Copyright 2005, American Chemical Society).

All previous works argued the adjustment of three factors to ensure a successful photoreduction DNA metallization: (i) DNA templates election; (ii) appropriate metal/DNA ratio to avoid free particles formation or known as background-generated nanomaterial; (iii) UV irradiation time, which relies on the light intensity as well as the metal ions reactivity to the light. However, this process also has a drawback, DNA can be damaged due to the prolonged UV light exposure, which affects the growth of the nanowire due to the loss of the capping ligands [22].

### 2.2.3 DNA metallization with a localized reducing group

To overcome the DNA bio-template destruction due to the chemical or photoreduction process, researchers take advantage of the rich chemistry of the DNA to achieve a clean, fast, and homogenous distributed metallization. A programmed metallization process can be achieved by the fascinating localized order of the DNA functional groups with almost non-background formation. In this case, DNA consequently plays a role as a template, capping legend, and a reducing agent. Until recent days, four main strategies to derivate the DNA strand with reducing groups.

2.2.3.1 DNA direct modification

In situ reduction and nucleation process can be achieved by direct modification of DNA strand with glutaraldehyde, where it can bind with the DNA primary amine groups in nucleobases (T, G, C, A) performing nucleation before metallization. The first report was revealed by Braun with co-workers when they used silver ions to perform the procedure [24]. The fascinating success sparks many researchers' enthusiasm to achieve the metallization with a more difficult DNA template structure. Branched DNA, DNA nanotubes, and DNA origami Figure 2. were reported recently [24–26].

The method has a direct impact on the metallization as the background almost disappears. Furthermore, the method reports a specialized programmable synthesis with highly specialized metal deposition. Following the same method, employing boranephosphonate for the same purpose have been reported by Caruthers with co-workers, where they reveal the ability of boranephosphonate (bpDNA) to reduce a variety of metals including $AuCl_4$, $PtCl_4$, and Ag^+ to form a metalized nanoparticles [27]. The compound poranephosphonate DNA is a DNA derived compound, where one of its nonbridging oxygen is replaced by a borane moiety (BH_3) [28,29]. Interestingly, since the BH_3 moiety is known as a reducing group; therefore, it is more convenient to use the bpDNA as both capping and reducing agent. The direct advantages of using bpDNA are: (i) the induction simplicity of the linkages to the DNA strands of interest (ii) bpDNA linkage reveals stability to all conditions; during the nanostructure's formation; (iii) maintaining homogeneity and site-specificity of metal deposition. However, regarding the synthesis difficulties of the modified DNA with (BH_3), the trials of taking the proposed approach into the application level have not been widened up to date.
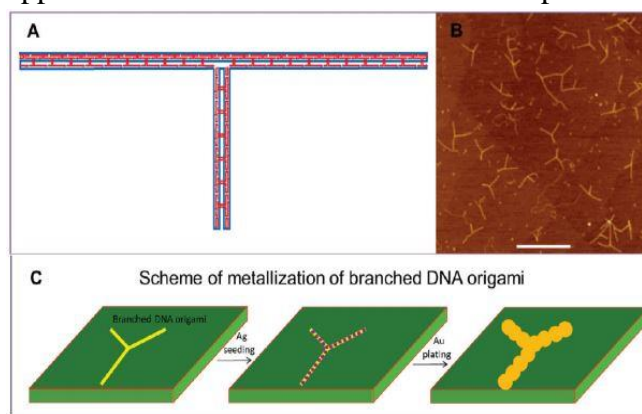
Figure 2: (A) Design of branched origami. (B) Branched origami deposited on the mica surface. Scale bar: 500 nm. Height scale: 4 nm. (C) Schematic illustration of DNA origami metallization (Adapted permission from Ref. [26], Copyright 2011, American Chemical Society.

2.2.3.2 Post-synthetic modification of DNA

The modification of DNA motifs with aldehydes opens up the way for many ideas to achieve different shape-controlled nanomaterials. A post-modification with a reductive species on the DNA can have also been studied by using PCR replicons, where metallization is reported in a programmable

manner [30]. Carell and co-workers reported demonstrating the aldehyde efficiency in the method. They succeed in obtaining the selective deposited silver ions grown on a post-modified DNA template with aldehyde groups [31].

2.2.3.3 Modified reductive ligands of DNA

The modification process of DNA is not that easy, as mentioned previously; therefore, efforts to achieve specific metallization without DNA modifications have been made. Recently, Takenaka with co-workers proposed a novel method for metallization selectivity of (dsDNA) by employing galactose derived naphthalene diimide (NDI) as a dsDNA reductive ligand [32, 33] their work considered acceptable for many researchers due to the ability to perform the process of metallization without any modification of the template.

2.2.4 Seed-mediated DNA metallization

DNA metallization has a limitation on the ion selectivity used to grow on its surface as discussed previously, therefore, to develop the proposed method and make it more reliable, researchers are trying to prepare metal nanoparticle with a cationic chemically modification on the DNA scaffold, the modified metal act as a seed to grow nanowires on it. The approach is employed to overcome the selectivity drawback and also to allow more complex metals structure to grow on a DNA template. Schreiber with co-workers proposed a gold NPs modified with amines, where the anionic DNA is electrostatically attached with cationic amines to form a seed for depositing of Au ions to further fabricate a continuously metalized structures with arbitrary shapes, as gold nano-cuboids and polymerized nanorods [34].

3. Multifaceted Applications

DNA can provide a flexible method to tune the growth of the nanomaterial construction, which provides a key success for shape-dependent physiochemical properties controlling. Furthermore, the rich of DNA chemistry provides the ability to interfere in many tasks as a targeting, capping, reducing agent, and recognition ability. Therefore, DNA templating growth of nanomaterial elucidates a massive value in many fields, such as environmental sensing, biosensing, nanoelectronics, bioimaging, therapeutics, and antibacterial use or catalysis.

3.1 Environmental sensing

Eco-systems and human health care are now requiring intensive efforts due to the high risk of environmental pollutants. Therefore, a fast, reliable, and eco-friendly analytical method is highly required to detect pollutants like gases, heavy metal ions, and other pollutants [50].

3.1.1 Heavy metal ions sensing

The tunable characteristics of DNA endow DNA itself advantage to serve for sensing purposes. Recently, DNA-templated metallic nanomaterials are used to fabricate electronic and optical probes for detecting environmental contaminants. Sensing of heavy metal ions was reported by Lu and co-workers, they utilized a helper oligonucleotide with long DNA fragments metalized with AuNPs for mercury (Hg^{2+}) selective sensing. They reported a rapid and highly selective optical sensing method even in the presence of other metal ions in aqueous solution [51]. However, Zeng and co-workers reported a label-free random dsDNA-templating CuNPs for Pb^{2+} sensing [52]. They reported that Pb^{2+} is selectively quenched the fluorescence of the CuNPs when introduced to the mixture. They supposed that the cause of sense is a direct interaction between Cu^+ and Pb^+ on the exposed

layer of copper nanoparticles rather than the interaction between the lead ions and the nucleic acid template. The proposed method is explained and summarized in Figure 3. Another approach has been proposed recently using electrochemical techniques including conductivity and resistivity for sensing purposes [53].
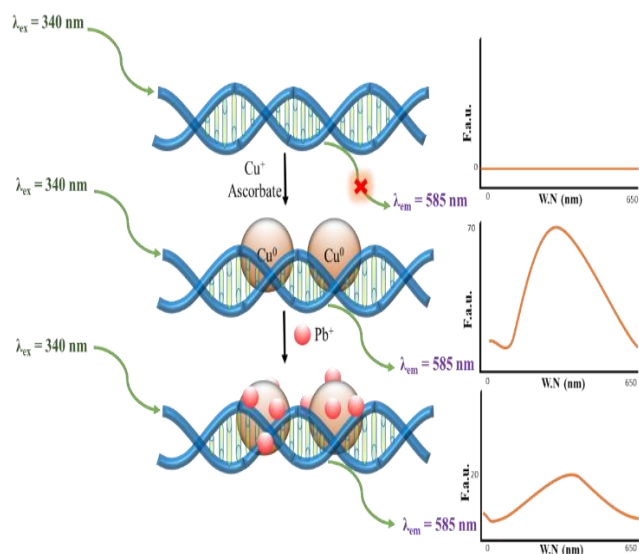
Figure 3: Schematic illustration represents the proposed protocol for the detection of label-free Pb^{2+} employing random dsDNA–CuNPs as a novel optical fluorescence probe.

3.1.2 Gas sensing

Gas detection is of high priority in everyday life or even in the industry. Toxic and explosive gases in the mining or industrial sectors have a high risk to handle, therefore, fast, reliable, and eco-friendly sensing method considered as a priority for many researchers [54]. As discussed earlier, DNA has an outstanding physicochemical property, which allows it to be also used in gas sensing. DNA is employed to tune the construction of the desired metal. To achieve a functional DNA-based sensor, the conductivity, impedance, or resistivity could be easily measured of the fabricated DNA-metallized

material, which will indicate the adsorption of the desirable sensing gas on the nanomaterial.

One of the most dangerous, toxic, and poisonous not only for humans but also for the eco-systems is the Ammonia gas [55]. Ammonia normally used in cooled system canning industries, fertilizers, and farming activities. Liu with co-workers employs silver nanowire with DNA-templated silver nanowires as a rapid sensor to detect ammonia gas even at low parts per million [56]. As a result of ammonia adsorption, silver nanowires' conductivity increased. The elevation of surface/volume ration of the Ag/DNA -templated nanowires, provides the material higher and faster adsorption criteria. Moreover, sensing can be done even in a room temperature compared to the previously proposed material, which makes the device more reliable and applicable in daily life [57].

3.2 Biosensing

DNA-template metallization also gains interest in biomedical research regarding the rich in functionality and flexibility of the metal itself and the DNA. High demand for fast and reliable analysis is required in recent days. Therefore, DNA-templated metal nanomaterial becomes popular in biomedical research [58–60]. However, the methodologies that had been reported are varied relying on the sensing mechanism including electrochemical impedance [61] sensing, or fluorescent detection Figure 4 & 5. a partial summarization is discussed related to the biosensing section. In the review, two approaches of nanomaterial behavior on the DNA-template, we tend to provide general principles to interested potential researchers aiming to provide help on the selection of the appropriate approach for DNA-templated metal nanomaterial-based biosensing.

3.2.1 Direct metallization on the DNA analyte

The proposed approach considered as a most reliable, simple, and direct approach among others in biosensing applications for the DNA metalized nanomaterials. The concept behind the approach is the use of a specific-dependent fluorescent of the proposed nanocluster material. A summarized approach is illustrated in Figure 4. There are two possibilities for the sensing mechanism on the approach. The probe can sense analytes by either changing the structure of the DNA template or interacting with the metal. The applications for the proposed approach are mainly in oligonucleotide-based biosensing to track down the mutations. For instance, Wang's group reported the employment of site-specific DNA that able to programing the growth of AgNCs to further utilized for detection of single nucleotide polymorphism (SNP) by measuring the photonic changes [62].
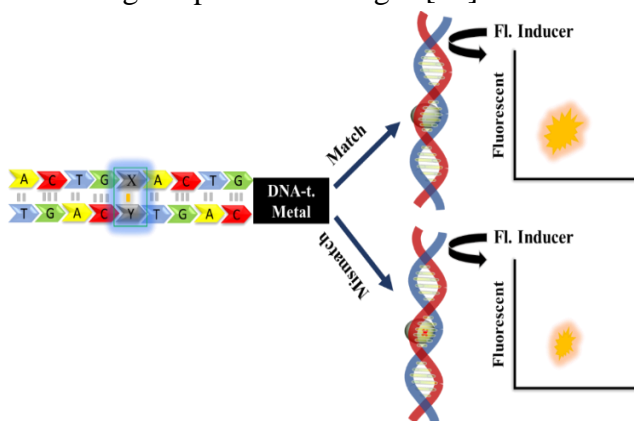
Figure 4: Schematic illustration summarized the direct metallization of the DNA analyte approach.

Using a similar approach, Hosseini's group works on epigenetic methylation detection on a DNA scaffold for early diagnosis of cancer [63]. Wang's group also employs the DNA-templated CuNCs nanomaterial to discriminate various (SNPs) [64]. The ability of fluorescent switching confirmation and its adjustable variation of the AgNCs provide the researcher advantages on structural fluctuation and dynamic solvation studies on the telomere sequences of the human genome [65]. Although the approach simplicity and reliability, it has a limitation for applications with non-DNA species. The approach is limited for sensing only DNA analytes that obtained a specified base sequence.

3.2.2 DE-metallization-based biosensors

A new investigation ongoing in the DNA-template metallization, reveals the outcomes of depositing metals on the DNA, which is enough to block all DNA biological and chemical functional groups [66] Recently, Chen with co-workers, reported that during tuning Ag^+ ratio with a short segmen of dsDNA or ssDNA, the biological functions of the DNA is completely blocked [67].

The same group also demonstrate different finding; they reported a compete for molecules that can knock out DNA due to the strong binding with silver, schematic illustration summarized the approach in Figure 5. For instance, Dopamine and biothiols are used to compete with the attachment with the DNA ligand and displace it from the deposited silver; therefore, the de-metallization process can be achieved by a competed molecule to knock out the DNA and replace it. They argued that the DNA biological functionality reserved, for example, found that ssDNA that demetallized by Dopamine is still functionalized and able to hybridized again [68]. However, what to establish an exact mechanism of DNA-de-metallization requires an in-depth investigation to reveals the real interaction between the DNA and the small legends.

3.2.3 Target-induced generation of metallization templates

The previous reposted methods sometimes are not able to recognize the analyte; for that,

researchers found a new approach, where a subsequent is generating to control the nanomaterial growth. The subsequent generations induced by the analyte, where finally the amplified nanomaterial's property is considered as metallization report.
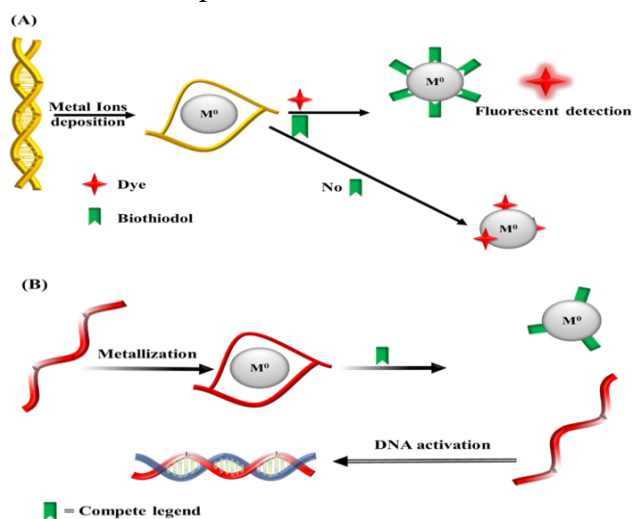
Figure 5: Schematic illustration summarized the biosensing-de-metallization approach. (A) Competing legend knocked out DNA and functionalized with a metal ion. (B) De-metallization and recycling process by the demetallized ssDNA.

The spark of this approach allows researchers to go forward with wonderful achievements. Song et al. reported a sensitive fluorescent approach to recognize ochratoxin A (OTA) in various food commodities [69]. The approach relies on the hybridization chain reaction (HCR), where an aptamer attached to dsDNA is acting as the analyte to further allow the adsorption of Cu ions on the DNA to form the cupper nanowire after digestion the dsDNA by exonucleases (Rec J_f). More recently, a dual amplification with a sensitive multicolor visual detection method had been reported by Xu with coworkers [70] to detect exosomes as a cancer biomarker. The method also relies on the HCR; however, this approach is

different from the previously reported, in this approach Figure 6, they used a dual amplification method to firstly achieve HCR then Au nanoshell is constructed due to the reduction amplification of the ascorbic acid. The most interesting finding is the ability of the naked eye distinguishing of the exosomes concentration due to the longitudinal blue shifting of the blue of the localized surface plasmon resonance peak.
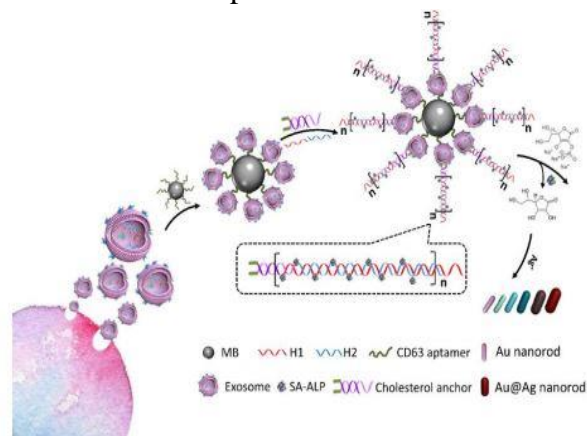
Figure 6: Schematic illustration of the mechanism for multicolor visual detection of exosomes based on HCR and enzyme-catalyzed metallization of Au NRs (Adapted permission from Ref. [70], Copyright 2019, American Chemical Society).

3.3 Other applications

Including the previously mentioned DNA-metallized nanomaterial's application, it is interfering with many other applications. Therapeutical trials for many diseases, like Alzheimer's and cancer [71] had been reported recently. Furthermore, the application of nanomaterials on microbial fields shows a promising outcome for the DNA-templated metals. As known to the majority, microbial infection is now ranked with a high consideration due to its high risk for humanity; the main issue is that many strains developed resistance against almost the majority of well-known antibiotics [72]. Surprisingly, DNA-templated metals, specially

AgNP$_s$, elucidate an antimicrobial effect against many microbial strains, Nanomaterial here is performing a targeted drug delivery, drug release controller, solubility enhancer, and immunity inhibitor [73,74]. The application of DNA-metallization in the therapy area is promising and has a bright future to overcome plenty of biomedical obstacles.

4. Conclusions

Impressive achievements have been accomplished over the last few years with the DNA-metallization and its applications, which is summarized as much as possible throughout this review. The DNA's fascinating biological and chemical functioning characters and the ability to self-assemble gave us a gift, leading to controlling the growth of metals. The programming of many metals' physicochemical and morphological characterization thus becomes more comfortable than previously reported. Hence, templating metals with DNA nanomaterials attracted attention in different disciplines for building up miniaturized devices. Nevertheless, as the research into DNA metallization is located at the interface of almost all fields, this approach considered extremely dynamic and will probably move on solving challenges and providing opportunities for outstanding breakthroughs in the near future.

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