The self-assembling of DNA-templated Au nanoparticles into nanowires and their enhanced SERS and catalytic applications†

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A simple photochemical technique is described for the synthesis of organized assemblies of Au nanoparticles (NPs) on a DNA template in a shorter time scale. The smaller Au nanoparticles (NPs) are initially formed in the DNA solution, self-assembled together, and generate the nanowire structures. The diameter and the length of the nanowires can be tuned by controlling the different reaction parameters. The average diameters of the individual Au NPs could be varied in the range of 10–50 nm, whereas their lengths could be extended to the level of several micrometres. The mechanism for the formation of the self-assembled structure of Au NPs on DNA is elaborated upon. The DNA–Au nanowire shows a highly stable and reproducible signal in surface enhanced Raman scattering (SERS) studies. The SERS activity was examined with Rhodamine 6 G (R6G) as a model dye molecule and the observed enhancement factor (EF) was \( \approx 10^6 \). The catalytic activity was tested for the reduction of 4-nitroaniline (4-NA) with sodium borohydride in aqueous solution. The synthesized Au nanowires were found to be stable for more than six months under ambient conditions at room temperature without any change of the optical properties. The superior SERS and catalytic activities of the material might be useful in future for different applications in organic catalysis reactions and in a variety of SERS based detections of bio-molecules, as sensors etc.

Introduction

Over the past few years, research into the self-assembled structure of nanoparticles (NPs) has attracted interesting attention due to their potential physical, chemical, and biological applications across the nanotechnological disciplines. During the past few years, several techniques have been developed for the generation of self-assembled NPs into ordered nanostructures.1,2 Among the different coinage metal NPs, Au NPs have received more attention due to their fascinating physical and chemical properties and promising applications in catalysis, nanoelectronics, sensors, photonics, biomedicine, and in surface enhanced Raman scattering (SERS) studies.3–7 The conjugation of NPs with biomaterials yielded ordered architectures that showed promising features in sensing and catalytic devices,8 nanocircuitry8 or SERS based signal amplifications.7 Bio-molecules have successfully demonstrated templating capabilities for a number of nanoscale materials. Different bio-molecules like nucleic acids, peptides, proteins, viruses or amino acids have been used for templating purposes.9–11 Among these various bio-molecules, the de-oxyribo nucleic acid (DNA) has been used as an inexpensive, well-characterized, controllable, and easily adaptable template whose physical and chemical properties can be explored to build inorganic nanostructures.4,8 Moreover, the intermolecular interactions in DNA are most readily programmed and reliably predicted; their versatile chemical structure makes them an effective genetic material for programming self-assembly.12,13 Due to its versatile nature, DNA was chosen as the preferential template in our present study. There have been several reports where researchers have assembled NPs into DNA for different types of applications. Mirkin et al. described a method for the assembling of colloidal Au NPs into nanoscopic aggregates using DNA as a linking element.14 Nanowires of other materials, like Ag,15 Au,14 Pt,16 Pd,17 Cu,18 Fe3O419 etc. have been metalized on a DNA template. Similarly, surface modified CdS NPs can be attached to DNA to form quasi-1D NP architectures.20 Deng and Mao reported the DNA templated fabrication of 1D parallel and 2D crossed metallic nanowire arrays using a

† Electronic supplementary information (ESI) available: The instruments used for the different characterizations and the corresponding sample preparation procedures are discussed. The detailed discussions for EDS, XPS analysis, the studies with other reactions parameters, calculations of the EF values, the figures related to UV-Vis, FE-SEM, EDS, XPS, different TEM images for the controlled experiments, 4-NA reduction origin plots and supporting table for catalysis are provided. This material is available free of charge via the internet, see DOI: 10.1039/c3ra42203h.

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molecular combing process for nanodevice construction.\textsuperscript{21} Mallouk and his group synthesized DNA directed Au nanowires on complexed DNA surfaces.\textsuperscript{22} Willner and his colleagues reported the Au NPs wires on DNA or polystyrene templates.\textsuperscript{23} The Schatz group reported the possible factors affecting the optical properties of DNA-linked Au NPs assemblies.\textsuperscript{24} It was reported that anisotropic NPs have interesting properties and can be widely used in catalysis, optics, and SERS studies.\textsuperscript{25,26} Au NPs have been used as an effective catalyst in different types of inorganic and organic catalysis reactions.\textsuperscript{27–32} The size and shape-selective catalysis reaction using Au NPs has been studied by Kundu et al. earlier.\textsuperscript{25,29} Recently, Huang et al. studied the catalysis reaction using Au NPs with dendritic structures as a catalyst.\textsuperscript{30} Apart from these catalysis reactions, Au NPs have been tested for SERS studies. In SERS, it is well understood that the plasmonic coupling effect at the nanometer gap junction between particles induces an enormous electromagnetic enhancement that allows the SERS signal to detect with single molecular sensitivity.\textsuperscript{31}

In this present study, we report a novel methodology for the synthesis of a self-assembled organized structure of Au NPs on a double-stranded DNA template by exploiting a simple photochemical route in a shorter time scale. The smaller Au NPs were initially formed in solution, self-assembled together, aggregated, and generated the DNA–Au nanowire structures. The synthesis was done by exposing the DNA–Au salt solution under UV light for about 4 h. The diameter and length of the nanowires could be tuned by controlling the various reaction parameters. The SERS activity of the DNA–Au nanowires was tested with R6G as a model dye molecule. The self-assembled structures of aggregated Au NPs on DNA generate a highly stable and reproducible SERS signal. The catalytic activity of the DNA–Au nanowires was examined for the reduction of 4-nitroaniline (4-NA) with sodium borohydride (NaBH\textsubscript{4}) in aqueous solution. To the best of our knowledge, there has been no previous reports on the formation of the self-assembled aggregated structure of Au NPs into nanowires on DNA by just 4 h of UV exposure and their superior activity in SERS and catalysis studies. The synthesized DNA–Au nanowires were found to be stable for more than six months under ambient condition at room temperature. The present process is simple, reproducible, straight-forward, highly cost effective, and robust.

**Experimental**

**Reagents and instruments**

Hydrogen tetrachloroaurate trihydrate (HAuCl\textsubscript{4}·3H\textsubscript{2}O, 99.9%) was purchased from Sigma-Aldrich and used without any further purification. Double-stranded DNA from Herrings testes with average size ~50 K bp (base pair) was purchased from Sigma-Aldrich. A Tris-EDTA buffer (pH ~ 7.4) was purchased directly from Sigma. 4-nitroaniline (4-NA) and several other nitro compounds were purchased from Balaji Scientific Company, Karaikudi, Tamil Nadu, India. Sodium poly (styrene) sulphonate (PSS) was purchased from Sigma-Aldrich. Sodium borohydride (NaBH\textsubscript{4}) was also purchased from Sigma-Aldrich and was freshly used daily for all of the catalysis reactions. Trisodium citrate dihydrate (Na\textsubscript{3}C\textsubscript{6}H\textsubscript{5}O\textsubscript{7}·2H\textsubscript{2}O, 99.99%) was purchased from Sigma-Aldrich and used as received. The dye molecule, Rhodamine 6 G (R6G, C\textsubscript{28}H\textsubscript{31}N\textsubscript{2}O\textsubscript{3}Cl) was purchased from Shree Shastha Enterprise, Karaikudi, Tamil Nadu, India. Ultrapure distilled (UPD) water, DNA\textsubscript{sc} and RNA\textsubscript{se} free was used for the entire synthesis process. The synthesized DNA–Au nanowire solutions were characterized using UV-visible (UV-Vis), high resolution transmission electron microscopy (HR-TEM), field-emission scanning electron microscopy (FE-SEM), Energy Dispersive X-ray Spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FT-IR), and surface enhanced Raman scattering (SERS) studies. In brief, the UV-photoirradiation was done with a UV-lamp (365 nm maximum wavelength) with a lamp power of 100 watt and working in 230 V–50 Hz. The distance of the sample stage from the light source was ~15–18 cm. The preparation of samples for the above measurements and the specifications of all the instruments used for their characterization, and details about the UV light source are discussed in detail in the supporting information.\textsuperscript{†}

**DNA templated synthesis of self-assembled aggregated Au NPs into nanowires under UV-photo-irradiation**

A stock DNA solution (1.23 × 10\textsuperscript{-4} M) was prepared by mixing a measured amount of DNA with Tris-EDTA buffer solution using DNA\textsubscript{sc} and RNA\textsubscript{se} free UPD water. The solution containing DNA in EDTA buffer was stirred using a magnetic stirrer overnight, which helps to get the homogeneous DNA solution without any pop-up of A and G bases in DNA. A stock solution of H\textsubscript{3}AuCl\textsubscript{4}·3H\textsubscript{2}O (10\textsuperscript{-2} M) was prepared and covered with black paper and stored in the dark to protect from sunlight. The Au(III) salt solution was mixed with a measured volume of DNA solution. Initially, after addition of Au(III) solution with DNA, they interacted, which was confirmed from the shift in the UV-Vis spectrum (not shown here). We changed the concentrations of DNA to Au(III) ions and prepared three different sets. For set 1, 10 mL of DNA solution was mixed with 0.20 mL of Au(III) solution. For set 2, 8 mL of DNA solution was mixed with 0.20 mL of Au(III) solution. For set 3, 10 mL of DNA solution was mixed with 0.35 mL of Au(III) solution. The resulting solution mixture was placed under UV light continuously for 4 h without any interruption. It was found that in the initial stage of the reaction (up to 90 min) the temperature of the solution mixture did not change much, although after 2 h of irradiation the solution became warmer (temperature ~ 40–45 °C). Finally at the end of the reaction after 4 h, the solution temperature nearly became ~50–52 °C. After the reaction was completed, the solution became pink to reddish pink to bluish pink in color depending upon the concentration of the reagents that confirmed the formation of Au NPs. The detailed concentrations of all the reagents, UV-irradiation time, and the average particle size etc. are given in Table 1.
Catalytic reduction of 4-NA using NaBH₄ and DNA–Au nanowires as a catalyst

The catalytic reduction of aromatic nitro compounds was tested with DNA–Au nanowires as a catalyst for the first time. The whole catalysis study was done with 4-NA as a specific example, although several other nitro compounds were also examined as a preliminary study. For a typical catalysis reaction, 4 mL of UPD water was mixed with 0.95 mL of (10⁻³ M) stock 4-NA solution and stirred for 5 min for homogeneous mixing. After that, 1 mL of 0.1 (M) ice-cold NaBH₄ solution was added and the mixture was shaken well. Finally, 0.05 mL of DNA–Au nanowire solution (from set 1) was added and the reaction was monitored using the UV-Vis spectrophotometer over different time intervals. The absorption spectra were recorded for every 2–3 min until completion of the reduction process. The total time required for the reduction was ~20 min and the light yellowish color of the 4-NA solution turned colorless due to the formation of the reduced product para-phenylenediamine (p-PDA) in the reaction medium. The completion of the reaction was confirmed from the change in color of the solution, as well as from the absorption bands in the UV-Vis spectrum. After the reaction was completed, the product was purified and the corresponding yield was measured.

Results and discussion

UV-Vis spectroscopic study

A mixture of Au(III) salt solution and DNA chains was exposed to UV light, which results in the nucleation of Au seeds that were grown automatically on DNA into bigger particles, which self-assembled together, aggregated, and generated the DNA–Au nanowire structures. Fig. 1 shows the UV-Vis spectrum of the solution mixture at the different stages of the DNA–Au nanowire synthesis. UV irradiation of only aqueous Au(III) salt solution generates Au particles with micrometre sizes which precipitated immediately due to the absence of any specific stabilizer. Moreover, the photoreduction of only aqueous Au(III) solution is slow, but it increases in the presence of specific organic ligands. The DNA–Au(III) solution mixture was photo-irradiated continuously for 4 h and resulted in a reddish pink color solution indicating the formation of Au NPs. The Au NP solutions show an additional band, along with the original DNA absorption band, in the range of λmax 520–550 nm due to the surface plasmon resonance (SPR) of the Au NPs. This SPR band shifted towards either the higher or lower wavelength side depending upon the size and shape of the particles. Fig. 1, curves C, D, and E show the SPR band of the Au nanowire solution at various DNA and Au(III) concentrations with a λmax of 529, 540, and 548 nm for sets 1, 2, and 3 respectively. This successive increase of the λmax value towards the higher wavelength side indicates the formation of larger sized Au particles. It was reported earlier by Jia and coworkers that when spherical Au NPs of smaller sizes aggregated to form linear chain-like structures, their SPR modes may interact and form new bands at higher wavelength regions. This is due to the interaction of their longitudinal mode of the plasmon oscillation along with the long axis of the Au NPs chains and they used siloxane surfactant for 1-D assembly of the Au NPs. In our study such types of SPR band were not observed, even in the higher wavelength side, as we did not observe any new plasmon bands even after scanning up to 1100 nm ranges. The resulting DNA–Au nanowire solution changes color from pink to reddish pink to bluish

| Table 1 Details of the concentrations of reagents, photo-irradiation time, and average diameter for the different sets of Au nanowires on DNA |
|---|---|---|---|---|---|---|
| Set No. | Final DNA conc. (M) | Final conc. of Au salt (M) | Time of UV irradiation (hours) | Color of the Au Nanowire solution with λmax values | Average diameter of the Au nanowires (nm) | Average diameter of the individual Au NPs (nm) | Approx. length of the chains |
| 1 | 1.20 × 10⁻⁴ | 1.96 × 10⁻⁴ | 4 | Pink (529 nm) | ~12 ± 3 | ~12 ± 3 | micrometre |
| 2 | 1.20 × 10⁻⁴ | 2.43 × 10⁻⁴ | 4 | Reddish Pink (540 nm) | ~65 ± 5 | ~30 ± 5 | micrometre |
| 3 | 1.18 × 10⁻⁴ | 3.38 × 10⁻⁴ | 4 | Bluish Pink (548 nm) | ~80 ± 10 | ~45 ± 5 | micrometre |

Fig. 1 The UV-Vis spectrum absorption spectra of the Au NPs arrays self-assembled into Au nanowires on DNA at different stages of the synthesis process. (A) is the absorption band of aqueous DNA solution; (B) is the absorption spectra of aq. Au(III) solution; and (C), (D) and (E) are the surface plasmon bands of the DNA–Au nanowire solution for set 1, set 2 and set 3 which show a λmax at 529, 540 and 548 nm respectively. The inset (C1, D1 and E1) shows photos of the three different colored DNA–Au nanowire solutions.
pink as indicated with the camera images in C1 (set 1), D1 (set 2), and E1 (set 3) respectively in the inset of Fig. 1. Moreover, as mentioned earlier, the optical properties of the synthesized DNA–Au nanowires were found to be stable for more than six months under ambient conditions when stored in a refrigerator in a sealed container. This can be confirmed from the color of the solution, as well as from the position of the SPR band in the UV-Vis spectrum (Fig. S-1, supporting information) which almost remained the same, as compared to the SPR bands for the as synthesized particles, as shown in Fig. 1.

**Transmission electron microscopy (TEM) and field-emission scanning electron microscopy (FE-SEM) analysis**

Fig. 2 shows the results obtained from the transmission electron microscopy (TEM) analysis for the self-assembled Au NPs that aggregated into Au nanowires in DNA. Fig. 2A and 2B

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**Fig. 2** Transmission electron microscopy (TEM) images of the self-assembly of Au NP arrays into Au nanowires on DNA at various reaction conditions. (A) and (B) show the low and high magnification TEM images of the Au nanowires on DNA for set 1 respectively. The insets of (A) and (B) show the corresponding higher magnification image and the selected area electron diffraction (SAED) pattern respectively. (C) shows the low magnification TEM image of the Au nanowires on DNA for set 2 and the corresponding inset shows the high magnification image. (D) shows the high magnification TEM image for set 2 at a different part of the sample and the corresponding inset shows the SAED pattern. (E) and (F) show the low and high magnification TEM images of the Au nanowires on DNA for set 3 respectively. The insets of (E) and (F) show their corresponding higher magnification images.
show the TEM images obtained from the set 1 DNA–Au nanowire solution. Fig. 2A shows the low magnification TEM image of the Au NPs where they self-assembled on the DNA chain into a linear fashion and generated the nanowires. The average diameters of the Au NPs on the DNA chain are ~12 ± 3 nm. The inset of Fig. 2A shows the corresponding high magnified image where it is seen that the densely decorated Au particles are on the DNA. The diameter of the Au particles is found to be consistent with the $\lambda_{\text{max}}$ value observed in curve C, Fig. 1. Fig. 2B shows the much higher magnified image of the DNA–Au nanowire taken from a specific part of Fig. 1A. From the image we can see that the Au particles are metalized on the DNA chain and produce the wire-like or pearl-like nanostructures. The inset of Fig. 2B shows the selected area electron diffraction (SAED) pattern which indicates the particles are single crystalline in nature. Fig. 2C and 2D show the TEM images from the set 2 Au NPs solution which correspond to curve D in Fig. 1. Fig. 2C shows the low magnified TEM image of the Au NPs where we can see individual Au NPs self-assembled on the DNA chain to generate a long nanowire. The average lengths of the Au nanowires are several micrometres. The inset of Fig. 2C shows the clear visual image of the Au particles and the average diameter of the individual Au particles are ~35 ± 5 nm. Fig. 2D shows the higher magnification image of the DNA–Au nanowire where the average diameter of the particles increases compared to set 1. All three sets of the particles are decorated along the DNA chain and generate the wire-like morphology. The inset of Fig. 2D gives the corresponding SAED pattern which indicates the crystalline nature of the particles. From Fig. 2C and 2D we can see that the average diameters of the DNA chains decorated by Au NPs are ~65 ± 5 nm. Fig. 2E and 2F shows the TEM images of the DNA–Au nanowires for set 3. The average length of the whole DNA chains decorated by Au NPs is a couple of micrometres. Fig. 2F shows the highly magnified image from the other part of the sample. The inset of Fig. 2F shows a much higher magnification image. The Au particles are formed with a much bigger size compared to set 1 and set 2 and the average diameter of the individual particles is ~45 ± 5 nm, whereas the diameters of the DNA chains decorated by bigger Au particles are ~80 ± 10 nm. From the images in Fig. 2D, 2E and 2F we can see the eventual diameter of the wires are not perfectly uniform as the Au particles grow un-uniformly along the side having pearl-like structures and there are nano gaps in between these structures. The uniformity of the DNA–Au wires is found to be reduced when the size of the individual particles increases from set 1 to set 3. So, from the TEM analysis we can see that the size of the individual Au particle are gradually increasing from set 1 to set 3 which matched well with the gradual shift of the $\lambda_{\text{max}}$ value towards the higher wavelength regions, as seen from Fig. 1. We did FE-SEM analysis to check the overall particles morphology with a larger scan area and the results are given in the supporting information† as Fig. S-2. As examples, we did analysis of the set-3, DNA–Au nanowire solution. From the low magnification analysis we can see many Au NPs aggregates are mixed with nanowires. While we focused for single nanowires at high magnification, we can see that the individual Au NPs are self-assembled and aggregated to from the wire-like DNA–Au nanostructures and the results matched with the TEM analysis.

Energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) analysis

Energy dispersive X-ray spectroscopy (EDS) analyses were used to check the elements present in the synthesized nanomaterials. Fig. S-3 (in supporting information) shows the EDS analysis for the DNA–Au nanowires solutions which consist of the expected elements present in the DNA–Au nanowires. The X-ray diffraction patterns of the self-assembled aggregated DNA–Au nanowires are shown in Fig. 3. The peaks were assigned to the diffraction from the (111), (200), (220), (311), and (222) planes of face-centered cubic (fcc) Au NPs that perfectly match with the other reports.28,40,41 The lattice constant is 0.4069 nm, which is within the error of the reported value (a = 0.4078), as given by JCPDS file no. 4-0784. According to the literature the shape of any nanocrystal is predominantly determined by the growth rate ratios along the (100) and (111) direction.42 In our present study we used DNA as a stabilizing agent and we also believe that the interaction of DNA with the different crystal facets of Au nanowire surfaces might have increased the growth rate along the (111) direction compared to the (100) direction. Although, at this point, we are not fully confirmed about this growth phenomenon and a detailed HR-TEM analysis with lattice fringe images might help us to support this point which will be discussed in the near future. A small hump in the XRD pattern at the lower 2θ range below 25° is also observed, which is probably due to the diffraction of crystalline DNA from the nanowire solutions.

X-ray photoelectron spectroscopy (XPS) analysis

The results obtained from the X-ray photoelectron spectroscopy (XPS) analysis are shown in the supporting information in Fig. S-4.† The survey spectrum in Fig. S-4, A, ESI† consists of the characteristic peaks from O (1s) at 529.9 eV, C (1s) at 283 eV, N (1s) at 397.1 eV and Au (4f). Fig. S-4, B, ESI† shows the
H bonds for the –CH2 group present in the DNA molecule. The spectrum A and B signify the asymmetric vibration of the C–\(^2\) region between \(3000 \text{ cm}^{-1}\). Absorptions in the 1500–1250 cm\(^{-1}\) region are caused by base sugar vibrations. The bands at 1498–1476 cm\(^{-1}\) are characteristic of the imidazolic ring vibration and the N7C8H bending of adenine and guanine was reported as \(1091 (1140–990) \text{ cm}^{-1}\). The peak at \(1091 \text{ cm}^{-1}\) on DNA due to the stretching vibration of the C–O–C or C–C group is shifted slightly to 1086 cm\(^{-1}\) after binding with the Au in DNA–Au nanowires. The region 790 cm\(^{-1}\) to 995 cm\(^{-1}\) in the FT-IR spectrum is mostly assigned to the de-oxyribose region on DNA.\(^{49}\) The peak at 925 cm\(^{-1}\) for pure DNA is shifted to 934 cm\(^{-1}\) for DNA–Au nanowires, clearly indicating the interaction of Au particles with the DNA molecule. In the lower wave number region from 625 cm\(^{-1}\) to 450 cm\(^{-1}\), shifting is observed when we compare pure DNA with DNA–Au nanowires. Similar types of shifting in the FT-IR spectrum was observed by Banay et al. in their study of Au NPs for the highly sensitive, level free detection of DNA.\(^{46}\) Our present result found similarities with other reports where Au NPs specifically bind with the backbone of N or O atoms, or with the phosphate groups in DNA.\(^{50,51}\)

Fourier transform infrared spectroscopy (FT-IR) analysis

Fig. 4 shows the FT-IR spectra of pure DNA and the DNA templated Au nanowires. The FT-IR spectra of pure DNA (curve A) and DNA templated Au nanowires (curve B) revealed that the Au particles are bound with the DNA. The peak at a higher wave number region at \(3725 \text{ cm}^{-1}\) for pure DNA is shifted to 3733 cm\(^{-1}\) for DNA–Au nanowires which is due to the stretching vibration of the hydroxyl group (–OH group) that came either from the water or from DNA.\(^{43}\) The peaks in the region between \(3000 \text{ cm}^{-1}\) and \(2840 \text{ cm}^{-1}\) in both the spectrum A and B signify the asymmetric vibration of the C–H bonds for the –CH2 group present in the DNA molecule. The carbonyl group stretching vibration (\(\nu (\text{C=O})\)) in both the spectra was observed at 1678 cm\(^{-1}\), which matched with the other reports.\(^{44,45}\) Two peaks at 2304 cm\(^{-1}\) and 1399 cm\(^{-1}\) are prominently observed for DNA–Au nanowires, which are not clearly observed for DNA itself, probably due to the binding of Au NPs with DNA. Absorptions in the 1500–1250 cm\(^{-1}\) region are caused by base sugar vibrations. The bands at 1498–1476 cm\(^{-1}\) characterized the imidazolic ring vibration and the N7C8H bending of adenine and guanine was reported as others have.\(^{46}\) In our study the bands at 1486 cm\(^{-1}\) in DNA were shifted to 1497 cm\(^{-1}\) for the DNA–Au nanowires which indicates that there is binding, probably between the N site of the guanine moiety in DNA with the Au NPs. The highly intense band observed in the region 1160–1310 cm\(^{-1}\) is mainly due to the oscillation of the sugar-phosphate group in DNA. The peak at 1174 cm\(^{-1}\) in pure DNA due to asymmetric stretching of the phosphate group is shifted towards 1209 cm\(^{-1}\) in the DNA–Au nanowires, indicating the attachment of Au NPs with the phosphate group of the DNA. The antisymmetric PO\(_2\) stretching band is a characteristic marker for backbone conformation that appears at approximately 1240 cm\(^{-1}.\(^{47,48}\)

### Table 2

<table>
<thead>
<tr>
<th>FT-IR frequency range (cm(^{-1}))</th>
<th>Absorbing bonds</th>
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<tbody>
<tr>
<td>3615, 3725 (3100–3750)</td>
<td>v (OH group in DNA/water)</td>
</tr>
<tr>
<td>1678 (1732–1595)</td>
<td>C–O, C–N, N–H(^{41})</td>
</tr>
<tr>
<td>1493 (1495–1480)</td>
<td>Bending ((\delta)) of the C–H bond in CH(_2)(^{44})</td>
</tr>
<tr>
<td>1306 (1170–1300)</td>
<td>Asymmetric stretching of the PO(_2) group</td>
</tr>
<tr>
<td>934 (800–1000)</td>
<td>De-oxyribose region</td>
</tr>
<tr>
<td>1091 (1140–990)</td>
<td>v (C–O–C, C–C)(^{44})</td>
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**Fig. 4** FT-IR spectra of the pure DNA from herring’s testes (curve A) and DNA–Au nanowire solution (curve B).
After UV exposure of the DNA and Au(III) mixture at 258 nm, which coincides with the DNA absorption peak, the Au(III) ions get reduced and produce small Au seed particles on the DNA. So, it can be indirectly proven that the UV-irradiation process is catalyzed by the DNA molecule from the two control studies. When we irradiated the Au(III) solution at 258 nm without the DNA, no stable Au NPs were formed. Similarly, when we irradiated the DNA and Au(III) mixture at a higher wavelength (320 nm) or lower wavelength (200 nm), which are away from the DNA absorption peak at 258 nm, no Au NPs were formed within our experimental time scale. So, the subsequent exposure of UV light for a period of 4 h gives stable Au NPs by the reduction of Au(III) ions with DNA. Moreover, the detailed impact of the UV-irradiation on the Au NPs size and shape has been discussed in the ‘study with other reaction parameters’ section with the necessary TEM images (as Fig. S-5, C and D) in the supporting information.

The complete reduction of Au(III) to Au(0) is a two photon process which takes place in the presence of UV light. It was reported earlier that different organic compounds, like poly (vinyl alcohol), TX-100, 2,7-dihydroxynaphthalene, poly ethylene glycol, having hydroxyl groups can be accelerated by the photo-reduction process. In our experiment the hydroxyl group present on DNA in the de-oxyribose sugar part may initiate the photo-reduction of Au(III) to Au(0). The nucleation of Au particles, their growth, and their stabilization after complete formation took place in the presence of UV light and DNA. Once the Au NPs were formed they stabilized on the DNA. We believe that the presence of N, O atoms or the phosphate back bone on DNA played an important role in the binding of Au NPs on the DNA surface, which can be further confirmed from the FT-IR analysis (details are given in the FT-IR analysis section). Once the Au NPs were formed in solution, they bound with the DNA chain, grew to a bigger size and finally self-assembled together to generate the aggregated DNA–Au nanowire structure. During the preparation of DNA solution we used a very low concentration of tris-EDTA buffer to get the homogeneous DNA solution without pop-up of A and G bases in DNA. It was reported by others that a relatively high concentration of EDTA can help to aggregate the CTAB (cetyltrimethylammonium bromide) capped Au nano rods by charge neutralization. However, such a type of aggregation did not take place in our case due to the similarity of charge for both DNA and EDTA. Moreover, we used the EDTA during the DNA solution preparation before the Au NPs were formed in solution and it only helps the pop-up of the A and G bases in DNA.

It was reported earlier that growth of Au NPs into ‘wire-like’ or ‘pearl-like’ morphologies generally took place due to their preferential binding along the (111) planes compared to the (100) planes and the growth ratio of the above planes finally determines the shape of the corresponding nanomaterials. So we also believed that in our study, the interaction of DNA with the different crystal facets of Au nanowire surfaces might increase the growth rate along the (111) direction compared to the (100) direction. Although, at this point, we have not fully confirmed this claim and further study with high resolution TEM with lattice fringe images will help us to establish this point in the near future. Now, with time, the individual Au NPs are closely packed as a dense structure on DNA and generate the wire-like or pearl-like structures. So, here DNA plays a dual role, it is used as a reducing agent for the reduction of Au(III) to Au(0) and also acts as a stabilizing agent after the formation of Au (0). The chain-like DNA double helix structure helps for the nanowire generation as we did not observe a similar type of structure when we used negatively charged poly (styrene) sulphonate (PSS) that also adsorbed at ~258 nm. The overall formation mechanism of the self-assembled aggregated Au

![Scheme 1](https://example.com/scheme1.png)

**Scheme 1** The overall reaction mechanism of the formation of Au nanowires on DNA from the self-assembled Au NP arrays.
NPs on DNA as nanowires is shown schematically in Scheme 1. From Scheme 1 we can see that initially Au(III) ions get reduced to produce smaller Au seed particles, then they grew on DNA and finally self-assemble to form the aggregated DNA–Au nanowire structure. Although, the native size of DNA is ~2–3 nm, once the Au particles nucleate over DNA, they grow in different directions preferentially towards the (111) plane and finally form the wire-like DNA–Au nanowire structures. The SPR band of the Au particles increases successively until the full reduction of the Au ions completed without a shift in the absorption maxima. This can be easily monitored from the UV-Vis spectra during the synthesis process (not shown here). Moreover, as discussed earlier, in the absence of DNA, no particles are formed in our experimental time scale. So all the control experiments described indirectly prove that DNA plays the most crucial role for the reduction of Au ions and their stabilization. Similar types of DNA templated Au NPs were prepared by chemical reduction of the DNA–Au(III) complex with hydrazine hydrate by Sohn et al. They observed that the diameter of the Au NPs ~45–80 nm and the individual Au NPs were embedded, and stabilized by the DNA molecule.

**Surface enhanced Raman scattering (SERS) study**

The discovery of SERS was done by Fleischmann et al. in 1974 and they studied the SERS effect over the rough Au particles surface. The plasmonic coupling effect at the nanometer gap junction between the particles induces enormous electromagnetic enhancement that allows the SERS signal to detect with single molecular sensitivity. Moskovits et al. suggested that the large enhancement resulted from the aforementioned electromagnetic effect in aggregates combined with either the intramolecular or metal-to-molecule or molecule-to-metal resonance. More recently, it has been believed that enhancement factor (EF) values above 10^7 and 10^8 may be able to detect single molecules. Although the problem arises due to poor reproducibility of ‘hot’ SERS active nanostructures, the lack of a quantitative SERS signal and the generation of a narrow distribution with high EF values remains unsolved.

In this study, we checked the SERS sensitivity with the self-assembled aggregated DNA–Au nanowires with R6G as the probe molecule of different molar concentrations, which was adsorbed on the nanomaterials surface. The concentration of the stock R6G dye solution was 10^−4 M for the SERS experiment and several other solutions were made by diluting the stock solution. We did the normal Raman spectra of only DNA and the DNA–Au nanowires solution (without the dye, R6G) and it was observed that there is a slight enhancement of Raman intensity for the DNA–Au nanowires solution compared to the pure DNA, as shown in Fig. 5. This slight increase of intensity might be due to the presence of Au nano-clusters on the DNA. All the peaks assigned in Fig. 5 are due to the presence of the aromatic base molecules (adenine, thymine, guanine, and cytosine) and the phosphate backbone on the DNA structure that matches with the other reports. The SERS experiment was carried out with the DNA–Au nanowire solution using R6G as the model dye molecule, as shown in Fig. 6. The chemical structure of the R6G molecule is shown in Fig. 6A where A1 and A2 show the camera images of the dye R6G itself and a mixture of R6G and the DNA–Au nanowires solution respectively. R6G was adsorbed on the DNA–Au nanowire surface by electrostatic interactions due to opposite charge of the dye (R6G, positively charged) and the DNA–Au nanowires (negatively charged surface due to phosphate backbone in DNA) solution. The charge dependent adsorption of R6G on Au NPs surface was studied in detail by Sang-Woo Joo et al., where they observed that negatively charged Au NPs adsorbed R6G much better compared to the positively charged Au NPs. Fig. 6B shows the Raman spectra of solid R6G and SERS spectra at different dye concentrations. We observed strong enhancement of the Raman signal, which is due to the C–C stretching of the aromatic ring (1649, 1615, 1575, 1509, 1363 cm⁻¹), C–O–C stretching (1313 cm⁻¹), C–H in plane bending (774 cm⁻¹), and C–C–C ring in plane bending (612 cm⁻¹). From Fig. 6 we can observe that the SERS intensity increases greatly when the concentration of R6G decreases from 10^{-4} M to 10^{-6} M. For the comparison study we made the dye concentration sufficiently high for measuring only the Raman spectrum. The enhancement factor (EF) in SERS can be calculated from the equation:

$$EF = \frac{I_{SERS}}{I_{RS}} = \frac{C_{SERS}}{C_{RS}}$$

Where, \(I_{SERS}\) = intensity of the enhanced SERS spectrum, \(C_{SERS}\) = analyte concentration in the SERS experiment, \(I_{RS}\) = intensity of the normal Raman signal and \(C_{RS}\) = analyte concentration in the normal Raman experiment. The highest EF value was 1.49 × 10^5 when we used R6G with a concentration of 10^{-6} M. The EF value calculated for the SERS peaks at 612, 1363 and 1615 cm⁻¹ were 4.54 × 10^5, 1.49 × 10^6 and 6.88 × 10^5 respectively. The detailed calculation of the EF value is given in the supporting information section. The EF value we observed was compared with other literature values and we can see that our aggregated self-assembled Au NPs on DNA as the substrate are comparable to most of the
Fig. 6 Surface enhanced Raman spectra (SERS) at different reaction conditions. (A) the chemical structure of the dye, Rhodamine 6 G (R6G); A1 and A2 are photos of the dye R6G and a mixture of R6G and Au NPs solution respectively; (B) the Raman spectra of only R6G and SERS of R6G adsorbed on the surface of DNA–Au nanowires at different concentrations; (C) size dependent SERS spectra of different sized Au NPs arrays in DNA–Au nanowire solutions.

other reports.\textsuperscript{59,62–72} Although, in a few cases, other researchers observed better EF values compared to our substrate.\textsuperscript{59,64} Fig. 6C shows the SERS spectra of R6G taking three different sets of DNA–Au nanowire solutions (set 1, set 2 and set 3 as given in Table 1) keeping the other parameters same. The average diameter of the individual Au NPs for the three different sets of Au nanowire solutions were $\sim 12 \pm 3$, $\sim 30 \pm 5$, and $\sim 45 \pm 5$ nm respectively. From Fig. 6C we observed that with the increasing size of the individual Au NPs on the nanowire chain, the intensity of the SERS is also increasing. The SERS intensity increases greatly when particle size increases from $\sim 12 \pm 3$ nm to $\sim 30 \pm 5$ nm and there is less increase when the particle size goes from $\sim 30 \pm 5$ to $\sim 45 \pm 5$ nm. It was observed previously that with the changes in particle size and shape, the SERS intensity also changed.\textsuperscript{63–65} The Kneipp group observed earlier that the SERS intensity changes when particle size was varied.\textsuperscript{66} They tested with spherical Au NPs in the size range 15–40 nm and observed that with an increasing Au NPs size, the SERS intensity also increases. In our experiment we also observed the same trend. The increasing SERS intensity happens mainly due to two things for the three different sets. First, the average particle size increases from $\sim 12 \pm 3$ to $\sim 45 \pm 5$ nm for set 1 to set 3. Secondly, for a single set, the individual particles aggregate over the DNA chains and those aggregated Au NPs self-assembled on DNA to generate the wire-like or pearl-like structure. So, the reason for the better SERS signal enhancement we observed from set 1 to set 3 might be due to the following two important particle arrangement related phenomena; one is the increase in particle size and the other is their aggregation. It was reported earlier that when NPs aggregate, they generate many numbers of ‘hot spots’ at the junctions of the aggregates, or in between the wire-like or pearl-like structures. The Plasmon coupling effect of the Au particles at these ‘hot spots’ will produce a very intense local electromagnetic field and consequently leads to a strong Raman cross-section enhancement.\textsuperscript{35} Similar types of Raman signal enhancement for aggregated Au NPs have been reported by several other researchers.\textsuperscript{67–72} In our experiment, we believed that the self-assembled aggregated DNA–Au nanowire structures are responsible for the generation of a highly stable and reproducible SERS signal. From the high magnification TEM images (in Fig. 2) we can clearly see that the diameters of the wires are not fully uniform, instead they formed wire-like or pearl-like structures having many numbers of nano gaps between them, which might be useful for the generation of suitable electric fields for Raman cross-section enhancement. Although, at this point we do not fully understand this phenomenon of enhancement of SERS intensity with the change in particles size and shape, further study will be carried out in future to identify their relationship.

Catalytic reduction of 4-NA using self-assembled Au NPs aggregated into nanowires on DNA as a catalyst

The efficiency of the DNA–Au nanowire structures were tested for the first time in a catalysis study of several organic nitro compounds using 4-NA as a model organic compound. The chemical reduction of 4-NA with only sodium borohydride is very slow. Only $\sim 4$–5% reduction takes place, even after aging the solution for 5 days as we observed from the UV-Vis spectrum (not shown here). This shows that the expected catalytic reaction does not take place in the absence of a catalyst even after 5 days, signifying that there exists a kinetic barrier, which prevents the electron transfer from the donor BH$_4^-$ to the acceptor 4-NA. It is important to mention that we did not observe any reduction of 4-NA taking place with only
native DNA solution (in the absence of DNA–Au nanowires) in our experimental time scale. Moreover, we did another control experiment where we checked the 4-NA catalysis reaction using a mixture of native DNA solution and excess NaBH₄ solution (without any DNA–Au nanowires). We did not observe any reduction of the 4-NA peak taking place, even when the solution mixture was kept for more than 2 days. However, with the presence of DNA–Au nanowire solution in the reaction mixture containing 4-NA and NaBH₄, the characteristic band of 4-NA was greatly reduced. So the presence of Au nanowires as a catalyst is extremely important for this catalysis reduction study.

For the catalysis study, we mixed 0.95 mL of 10⁻³ (M) 4-NA solution with 4 mL of UPD water and 1 mL of 0.1 (M) NaBH₄. Finally 0.05 mL of DNA–Au nanowire solution (set 1) was added, with the further details given in the experimental section. The reduction of nitro compounds using spherical or anisotropic noble metal NPs as a catalyst was studied earlier. The pH of the 4-NA solution (10⁻³ M) is 6.15 and the pH of NaBH₄ solution (10⁻¹ M) is ~10.6. The pH of the mixture of 4-NA and NaBH₄ was ~10.2. The UV-Vis absorption peak of 4-NA appears at 379 nm due to intermolecular charge transfer within 4-NA. It is well-known that metal NPs can catalyse the chemical reaction by electron transfer and remove the kinetic barrier. The progress of the reduction can be monitored in situ spectrophotometrically by the reduction of the absorption peak of 4-NA at 379 nm with time. Fig. 7A shows the time dependent successive reduction curve for the reduction of 4-NA. Each spectrum was recorded at an interval of 2–3 min. The 379 nm peak decreases gradually and a new peak at 237 nm appears and its intensity increases gradually due to the formation of reduced product p-PDA in the reaction medium. The inset of Fig. 7A shows two differently colored solutions (one is a yellowish color 4-NA and the other is colorless p-PDA). The absorption peak at 379 nm nearly disappears in 20 min, suggesting that the reaction is complete. As we used NaBH₄ concentration in large excess in the reaction, its concentration can be considered as constant throughout the reaction and pseudo-first order kinetics can be applied with respect to 4-NA reduction. Fig. 7B shows the origin plot of ln ([C]/[C₀]) vs. time (T, min), from which we can see that our reaction followed pseudo-first order kinetics with respect to 4-NA. The rate constant value obtained from the linear ln ([C]/[C₀]) vs. time (T, min) plot for 4-NA reduction (Fig. 7B) is 9.09 × 10⁻² min⁻¹ and the correlation coefficient and standard deviation values are 0.98 and 0.126 respectively. The pseudo-first order rate equation is ln [C] = 0.090 × t + ln [C₀], where C is the concentration at time t (min) and C₀ is the initial concentration. The related concentration values were converted from the 4-NA absorbance values at 379 nm as per the pre-determined calibration curves, as shown in the Supporting Information as Fig. S-6. Fig. S-6, part (A), ESII shows the concentration dependent absorption spectra of aqueous 4-NA and NaBH₄ mixture and part (B) shows the calibration plot of absorbance vs. concentration of 4-NA. From Fig. S-6 (B), ESII the correlation coefficient value we got, which is near to unity, supports our assumption of considering the 4-NA reaction as having pseudo-first order rate kinetics. Similar types of results were obtained by Wang and his colleagues during their study of 4-nitrophenol (4-NP) reduction using metal loaded oxide nanospheres as the catalyst.⁷₃ The yield of the product is calculated, which is almost near to 100%. Apart from set 1, we also checked the catalysis reaction using the set 2 and set 3 DNA–Au NP solutions. We have seen that the catalytic reaction rate increases from set 1 to set 2 to set 3. We also calculated the turn over number (TON) of the catalyst. In heterogeneous catalysis, the TON is calculated as the ratio of the % of yield multiplied by the amount of reactant molecules and with the amount of catalyst used. The reaction yields, number of Au particles used in catalysis, TON etc. are summarized in Table S-1 in the supporting information. From Table S-1, ESII we can see that the TON increases from set 1 to set 3 of the DNA–Au NPs solutions which are consistent with the increasing catalytic rate from set 1 to set 3, as discussed earlier. We have counted all the Au atoms, not only the surface atoms, for calculation of the TON. Although this kind of calculation will be more meaningful for practical applications, as the catalysts are usually so expensive that every atom should be considered. The formation of the final product was confirmed from the UV-Vis spectrum and also from the ¹H NMR and Co-TLC studies (not shown here). From the NMR

![Fig. 7 UV-Vis absorption spectrum for the different stages of the catalysis reaction using DNA–Au nanowires as catalyst. (A) is the successive decrease of the absorbance value for the reduction of 4-NA (at 379 nm); (B) shows the ln (Abs) vs. time (T) plot for the reduction of 4-NA (at 379 nm) at different times.](image-url)
spectrum we observe peaks at \( \delta \) values of 6.58 for the aromatic proton, 4.25 for the amino proton and 7.25 for the solvent. We used borohydride concentration in large excess compared to 4-NA or compared to the nanowires solution. The excess borohydride might increase the pH of the solution, prevent its degradation and helps to clean the air by liberating hydrogen, so the unwanted air oxidation of the final product is eliminated.

The catalytic efficiency of the DNA–Au nanowires calculated is rather high compared to other materials reported for similar types of reaction using either spherical or anisotropic Au NPs. The details of the other methods used to prepare Au nano components, their shapes and catalysis reaction rates are summarized in Table 3. From Table 3, we can clearly see that the catalysis reaction rate is higher in our present method compared to others. It is well known that catalytic activities are mainly determined by two key parameters, one is the availability of active surface area and the other is the catalyst active sites on the surface. Additionally, high indexed facets can also improve the catalytic properties of nanomaterials, as reported by others. This self-assembled aggregated nanowire structure shows a very high surface-to-volume ratio and the widely exposed active surface of the aggregated nanostructures provides an active site for selective adsorption and is helpful for the catalytic reaction. Apart from these factors, the self-assembled aggregated Au nanowires are not fully uniform (as confirmed from TEM analysis), rather they grow as ‘pearl-like’ structures (discussed earlier in the TEM analysis and mechanism section) which have a higher number of corners and edges atoms (low coordination gold atoms) on the DNA–Au nanowire surface. It has also been reported that the dendritic structure of Au NPs have a higher number of edges and corners which might increase the catalytic reaction rates. So, due to all these factors, in the case of self-assembly, the catalytic activity of the DNA–Au nanowires is significantly enhanced.

**Table 3** Comparison of the catalysis rates with other literature reports with our present method

<table>
<thead>
<tr>
<th>Name of the stabilizing agent</th>
<th>Types</th>
<th>Nano component</th>
<th>Shape of the NPs</th>
<th>Rate constant ((\text{min}^{-1}))</th>
<th>Reference number in this paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB (Cetyl trimethyl ammonium bromide)</td>
<td>Surfactant</td>
<td>Au</td>
<td>Nano Rod</td>
<td>2 (\times) 10^{-2}</td>
<td>25</td>
</tr>
<tr>
<td>Decane-1,10-bis(methylpyrrolidinium bromide)</td>
<td>Surfactant</td>
<td>Au</td>
<td>Nano Rod</td>
<td>1.9 (\times) 10^{-2}</td>
<td>30</td>
</tr>
<tr>
<td>1-dodecyl-3-methylimidazolium bromide</td>
<td>Ionic liquid</td>
<td>Au</td>
<td>Nano Rod</td>
<td>4.4 (\times) 10^{-2}</td>
<td>75</td>
</tr>
<tr>
<td>Citrate-polystyrene</td>
<td>Anion exchange resin</td>
<td>Au</td>
<td>Spherical</td>
<td>(\sim) 1 (\times) 10^{-2}</td>
<td>76</td>
</tr>
<tr>
<td>Azacyclon</td>
<td>Polymeric amines</td>
<td>Au</td>
<td>Spherical</td>
<td>(\sim) 1 (\times) 10^{-2}</td>
<td>77</td>
</tr>
<tr>
<td>PAMAM</td>
<td>Dendrimers</td>
<td>Au</td>
<td>Spherical</td>
<td>1.8 (\times) 10^{-2}</td>
<td>78</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>Inorganic reducing agent</td>
<td>Au</td>
<td>Spherical</td>
<td>2.06 (\times) 10^{-2}</td>
<td>79</td>
</tr>
<tr>
<td>Tri-sodium Citrate</td>
<td>Citric acid series</td>
<td>Au</td>
<td>Spherical</td>
<td>2.68 (\times) 10^{-2}</td>
<td>80</td>
</tr>
<tr>
<td>Deoxyribo nucleic acid (DNA)</td>
<td>Bio-molecule</td>
<td>Au</td>
<td>Au NPs aggregated as wires</td>
<td>9.09 (\times) 10^{-2}</td>
<td>Present method</td>
</tr>
</tbody>
</table>

*Note: The values are approximate and may vary slightly depending on the experimental conditions.*

**Scheme 2** Formation of the self-assembled Au nanowires on DNA, their catalytic and SERS activity.
assembled aggregated DNA–Au nanowires, the chance of inter-particle electron transfer becomes much higher, which in-turn increases the catalysis reaction rate. Moreover, the preferential wire-like arrangement on DNA can help give a better and faster electron relay from the donor BH$_4^-$ to the acceptor 4-NA and the corresponding reduction takes place at a faster rate. The overall formation of the DNA–Au nanowires and their application in catalysis and SERS studies are schematically shown in Scheme 2. The catalysis reactions using DNA–Au nanowires as a catalyst were found to be extremely efficient, straightforward, reproducible, and robust. Moreover, we also checked the stability of the catalyst by aging for different times. We have seen that the DNA–Au nanowires as a catalyst can be useful for several times once more 4-NA is added to the reduced solution and the catalyst can be re-used for a couple of times, although the catalytic efficiency is reduced a bit after a few cycles. Apart from 4-NA, we also conducted some preliminary studies with other nitro compounds and observed that the full reduction is completed in a reasonably lower time scale. The detailed work with other nitro compounds will be discussed in the near future. So the enhanced catalytic rate in the present report will certainly become advantageous in terms of applications and cost effectiveness of the materials.

Conclusion

In summary, we have demonstrated a new route for the synthesis of self-assembled Au NPs aggregated into nanowire structures on a DNA template using a simple photochemical approach. The DNA–Au nanowires were synthesized by mixing a proper concentration of DNA with Au salt and passing UV light continuously for a period of 4 h. The diameters of the individual Au NPs were varied in the range of 10–50 nm, whereas their length can be extended into the micrometre range. The eventual diameter of the particles can be tuned by controlling the various reaction parameters. The potentials of the DNA–Au nanowires were examined with SERS study and in a catalytic reaction. The SERS experiment was conducted taking R6G as a model dye molecule in the presence of different sized DNA–Au nanowires solutions. From the SERS experiment we observed an EF value ~10$^4$, which might find potential applications in the SERS based detection of single molecules. The catalysis reaction was tested using different organic nitro compounds. The catalytic activity of the DNA–Au nanowires was found to be superior compared to other reported methodologies and the process of catalysis is simple, straightforward, reproducible, and robust. So, this enhanced SERS and catalytic application of the DNA–Au nanowires opens up new avenues for reliable quantitative SERS studies in in vitro biosassays, in situ probe tracking in cells, in vivo/ex vivo Raman imaging, NPs based photothermal therapeutics, and might be useful for several other organic catalysis reactions in the future.

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