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Supporting Information's for

Self-assembling of DNA-templated Au Nanoparticles into Nanowires and their enhanced SERS and Catalytic Applications

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Experimental Section

Instruments used for characterization

The self-assembled aggregated DNA-Au nanowires were characterized with several spectroscopic techniques as discussed below. The high resolution transmission electron microscopy (HR-TEM) analysis was done with a Tecnai model TEM instrument (Tecnai^{TM} G2 F20, FEI) with an accelerating voltage of 200 KV. The Energy Dispersive X-ray Spectroscopy (EDS) analysis was done with a separate EDS detector incorporated with the same TEM instrument. The UV-visible (UV-Vis) absorption spectra were recorded in a Hitachi (model U-4100) UV-Vis-NIR spectrophotometer equipped with a 1 cm quartz cuvette holder for liquid samples. The Field-emission Scanning electron microscopy (FE-SEM) images are done with Carl Zeiss SEM instrument (model number: Supra 55VP/41/46) with an accelerating voltage between 20 kV using SE or Inlens detector. The resolution of the instrument was 0.8 nm. A thin film of the DNA-Au nanowires was made in a glass substrate and the fabricated thin films were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier Transform Infrared Spectroscopy (FT-IR) analyses. The XRD analysis was done with a scanning rate of 0.020 s^{-1} in the 2θ range of 10-90° using a PAN analytical Advanced Bragg-Brentano X-ray powder diffractometer (XRD)

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with Cu Kα radiation (λ = 0.154178 nm). The XPS analysis was carried out using an ESCA model VG 3000 system X-ray photoelectron spectrometer with monochromatic Mg Kα line (1253.6 eV) radiation. The instrument integrates a magnetic immersion lens and charge neutralization system with a spherical mirror analyzer, which provides real time chemical state and elemental imaging using a full range of pass energies. The emitted photoelectrons were detected by the analyzer at a passing energy of 20 eV with energy resolution of 0.1 eV. The incident X-ray beam was normal to the sample surface, and the detector was 45° away from the incident direction. The analysis spot on the sample was 0.4 mm × 0.7 mm. The overall energy resolution was about 0.8 eV. Samples for the survey spectrum was recorded in the 0 – 700 eV kinetic energy by 1 eV steps, where as high resolution scans with 0.1 eV steps were conducted over the following regions of interest: Ag 3d, N1s and C 1s. The FT-IR analysis was done with the model Nexus 670 (FTIR), Centaurms 10X (Microscope) having spectral Range 4,000 to 300 cm^{-1} with a MCT-B detector. Surface enhanced Raman scattering (SERS) study was done with Lab RAM HR (Jobin Yvon) and Renishaw inVia Raman Microscope using an excitation wavelength of 488 nm (Ar ion laser) and 633 nm (He-Ne laser) respectively. The excitation light intensity in front of the objective was ~10 mW with a spectral collection time of 1 sec for both Raman and SERS experiment. The integration time for our measurement was set to 10 sec. The approximate diameter of the laser spot falls on the substrate is ~ 1 μm. The UV-photoirradiation was done with a UV-lamp (UVP-Black Ray model, B-100A, AP High Intensity UV lamp, 365 nm maximum wavelength) having a lamp power of 100 watt and working in 230 V – 50 HZ. The average illumination intensity of the UV light was ~ 13 mW/cm^2 and the maximum photon flux density was 12 μmol photons m^{-2} s^{-1}. The distance of the sample stage from the light source was ~ 15-18 cm. The sample solution was kept over a plastic box such that the UV light falls directly onto the sample solution.

Preparation of samples for various characterizations

The DNA-Au nanowire solutions were characterized using UV-Vis, TEM, FE-SEM, EDS, XRD, XPS, FT-IR, and SERS measurements. The aqueous DNA-Au nanowire solution was used for the measurement in UV-Vis spectrophotometer. The samples for TEM were prepared by placing a drop of the corresponding DNA-Au nanowire solution onto a carbon coated Cu grid followed by slow evaporation of solvent at ambient conditions. The EDS

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analysis was done during the TEM analysis from the same instrument. For XRD, XPS, and FT-IR analysis, glass slides were used as substrates for thin film preparation. The slides were cleaned thoroughly in acetone and sonicated for about 25 min. The cleaned substrates were covered with the DNA-Au nanowire solution and dried in air. After the first layer was deposited, subsequent layers were deposited by repeatedly adding more DNA-Au nanowire solution and drying. Final samples were obtained after 6-8 depositions and then analyzed using the above techniques. For FE-SEM, the samples were prepared on glass substrate similar way but only a single deposition was done to get monolayer of the particles. It is important to be note that, for FE-SEM study, we used the Au NPs solution directly after synthesis without separation to see overall morphology of the sample as synthesized condition. Although, for TEM analysis, SERS study or for catalysis reaction we used only the nanowire solution as we separated them from the mixture of Au NPs aggregates via controlling the time and speed of centrifugation. That can be confirmed from the TEM analysis (see Figure 2, main text) where we observed mostly the nanowires. The sample for SERS measurement was prepared by mixing a measured volume of DNA-Au nanowire solution with R6G and deposited over a glass slide and dried.

Energy Dispersive X-ray Spectroscopy (EDS) analysis

Energy dispersive X-ray spectroscopy (EDS) analysis was done to check the elements present in the corresponding nanomaterials solution. Figure S-3 shows the EDS analysis for the DNA-Au nanowires which consists the expected elements present in the DNA-Au nanowires. The spectrum consisted of peaks from C, Cu, Au, P and N. The high intense C and Cu peak came from the C-coated Cu TEM grid used for the TEM analysis. The Au peak came from the DNA-Au nanowires, whereas P and N peaks came from DNA that was used as the template for Au nanowire synthesis, which confirms the presence of Au on the DNA surface.

X-ray Photoelectron Spectroscopy (XPS) analysis

The results obtained from the X-ray photoelectron spectroscopy (XPS) analysis are shown in Figure S-4 The sensitivity of XPS makes it an excellent tool for chemical analysis for its ability to resolve the chemical identities of the atoms from the measured electron

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binding energies. Figure S-4, A, B, C, and D shows the XPS spectra for overall survey (A), Au (4f) (B), C1s (C), and N (1s) (D) for the self-assembled Au nanowire films on the glass substrate. The survey spectrum consists the characteristic peaks from O (1s) at 529.9 eV, C (1s) at 283 eV, N (1s) at 397.1 eV and Au (4f). The O (1s), C (1s), and N (1s) peaks came from the DNA and Au (4f) peak came from the Au nanowires. Figure S-4, B shows the XPS spectrum analysis for Au (4f) regions. From the spectrum we can see that it is characterized by a doublet which arises due to spin-orbit coupling ($4f_{7/2}$ at 88.54 eV and $4f_{5/2}$ at 92.3 eV) of Au (4f). Figure S-4, C and D show the spectral deconvolution of the C (1s) and N (1s) peaks respectively.

Study with other reaction parameters

In our experiment we have examined the effects of different reagent concentrations for the synthesis of self-assembled aggregated DNA-Au nanowires. We varied the concentration of DNA, Au (III) solution, UV-irradiation time, and tested with free DNA bases. The control experiments demonstrated that the self-assembled Au nanowires are formed at a specific concentration, as given in Table 1 in the main text. When increasing the concentration of Au(III) $\geq 10^{-1}$ M, as indicated by the blue color solution but get precipitated due to the aggregation of the Au NPs on DNA (supporting Figure S-5, A). By increasing the DNA concentration to a very high value of ~ 10^{-2} M, similar types (like Figure S-5, A) of aggregated nanostructures are observed (not shown here). When we used free DNA bases, instead of nanowires only the spherical Au NPs are formed as shown in the supporting Figure S-5, B. The role of UV-irradiation on the morphology of the synthesized Au-NPs mainly size, shapes were studied in detail. We have seen that 4 hour UV irradiation time is sufficient for the complete formation of Au NPs on DNA under our experimental condition. Shorter UV irradiation duration (~1.5-2 hour) gives Au NPs with branched structure but not long wires as shown in supporting Figure S-5, C. When we irradiate for a longer period of time (~ 8-10 hour), Au nanowire was formed but they aggregated and mixed with other branched NPs structures as shown in supporting Figure S-5, D. A summary of the results shows that aggregated Au NPs formed the wire-like structure on DNA for the specific concentrations given in Table 1 in the main text.

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Calculation of Enhancement Factor (EF) value in SERS

The concentration of the stock probe molecule used for SERS study was 10^{-6} (M). We used 500 µl of it and final volume was 1000 µl. So the final concentration of the probe was 5×10^{-7} (M).

So, 1 litre of 5×10^{-7} mole contains 6.023×10^{23} number of molecules.

Then, 1000 ml of 5×10^{-7} mole contains 6.023×10^{23} number of molecules.

Then, 1 ml of 1 mole contains 3×10^{14} number of molecules.

So the 1 µl of the same solution contains 3×10^{11} number of molecules.

For deposition on substrate, we take 10 µl solutions, so it contains 3×10^{12} number of molecules.

When we deposit 10 µl solutions, it approximately covers 3 mm circular area on the substrate. So the diameter is 3 mm = 3×10^{3} µm.

So the number of molecule per µm area = $3 \times 10^{12} / \pi (3/2 \times 10^{3})^2$

$= 4.24 \times 10^{5}$, so calculated $\mathbf{C_{SERS} = 4.24 \times 10^{5}}$

The approximate diameter of the LASER spot = 1 µm and the number of molecule inside the LASER spot ($\mathbf{C_{SERS}}$) = $\mathbf{4.24 \times 10^{5}}$

For calculation of $C_{RS,}$ we used 10^{-2} (M) probe solution and in similar way when we calculate the number of molecule per µm area ~ 10^{9}.

So the calculated $\mathbf{C_{RS}}$ **is** = $\mathbf{10^{9}}$

Now if we calculated the EF for the peak position at 1363 cm^{-1} using the following equation,

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

It will be, $$\mathbf{EF} = \frac{\mathbf{8219/4.24 \times 10^{5}}}{\mathbf{13/10^{9}}} = \mathbf{1.49 \times 10^{6}}$$

So the EF value at peak position 1363 cm^{-1} is $\mathbf{1.49 \times 10^{6}}$.

In similar way, the EF values for other peak position were also calculated.

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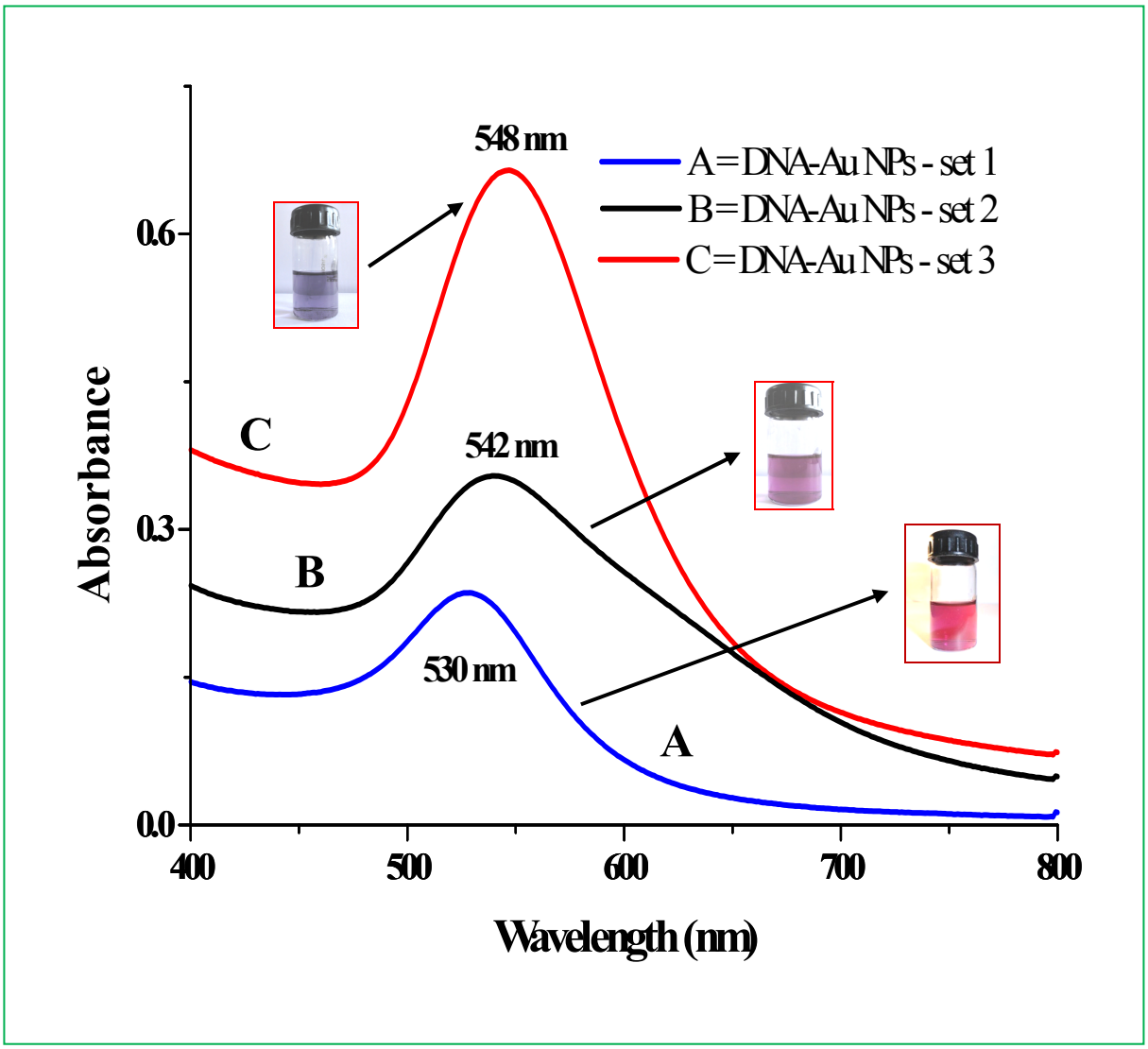

Figure S-1. The UV-Vis spectrum absorption spectra of DNA-Au NPs after 6 month of aging. (A), (B) and (C) are the SPR band of DNA-Au nanowire solution for set 1, set 2 and set 3 shows a λ_{max} at 530, 542 and 548 nm respectively. Inset shows the color of the different sets after 6 months.

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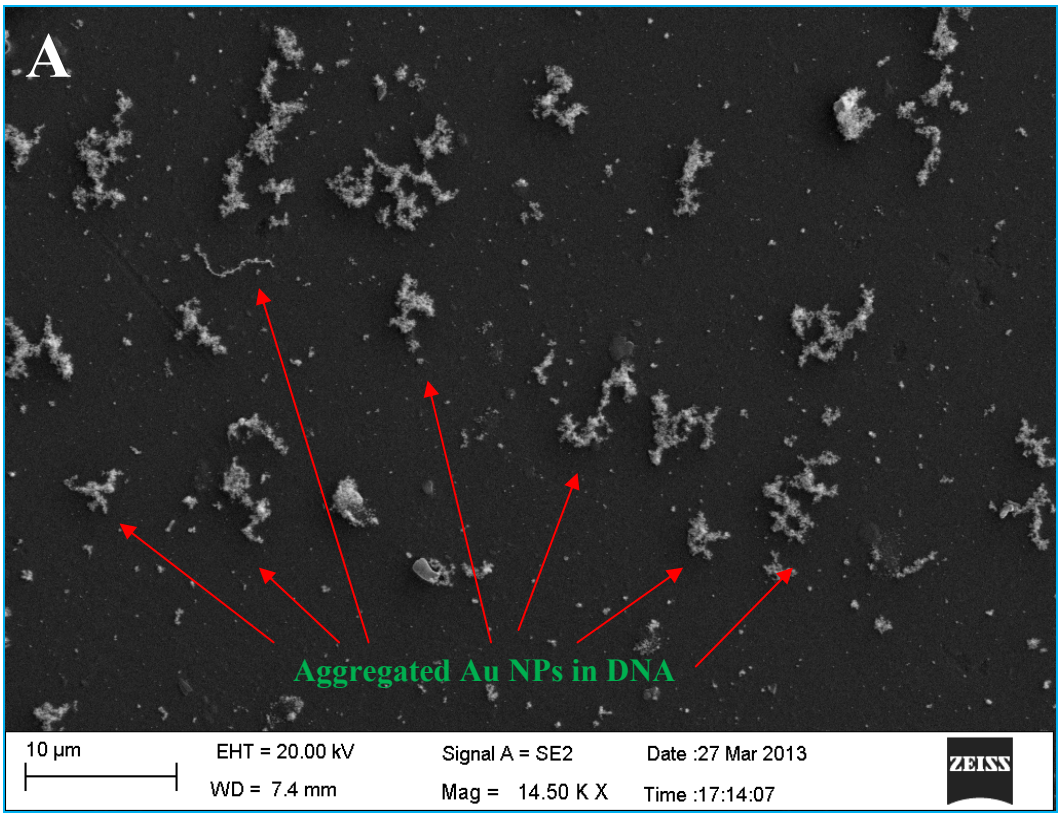

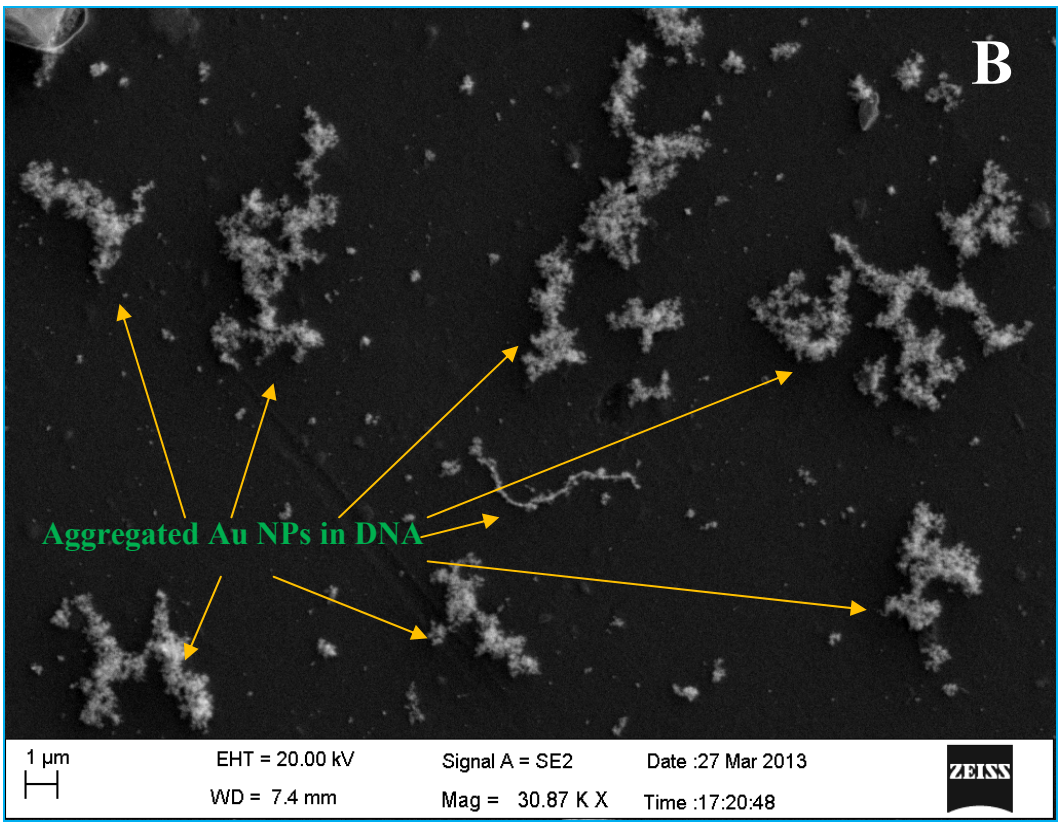

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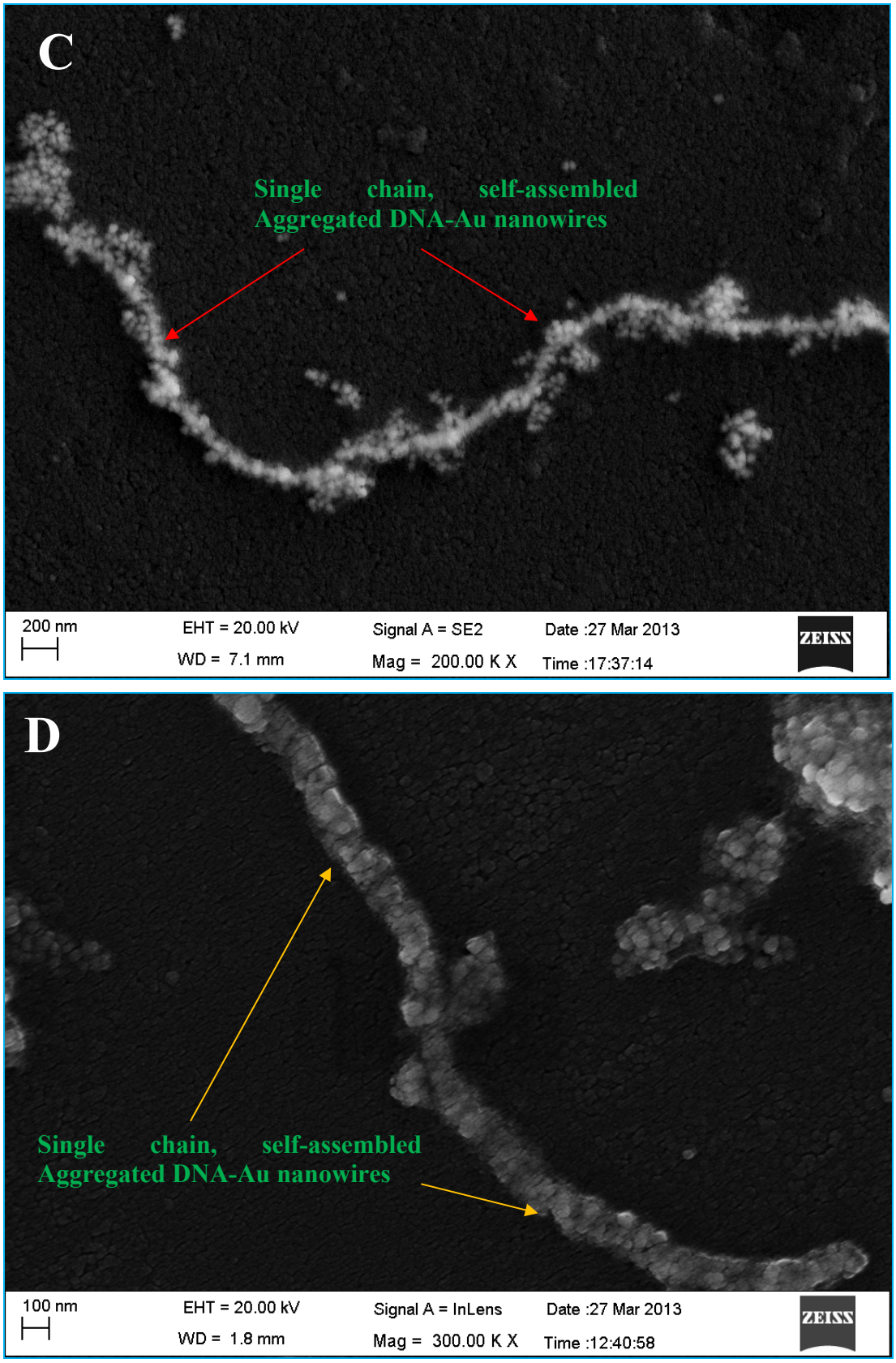

Figure S-2, A-D: The FE-SEM images of self-assembled aggregated DNA-Au nanostructures at different magnification. (A) and (B) shows low magnified images with lots of aggregates and (C) and (D) shows the high magnified image of single aggregates.

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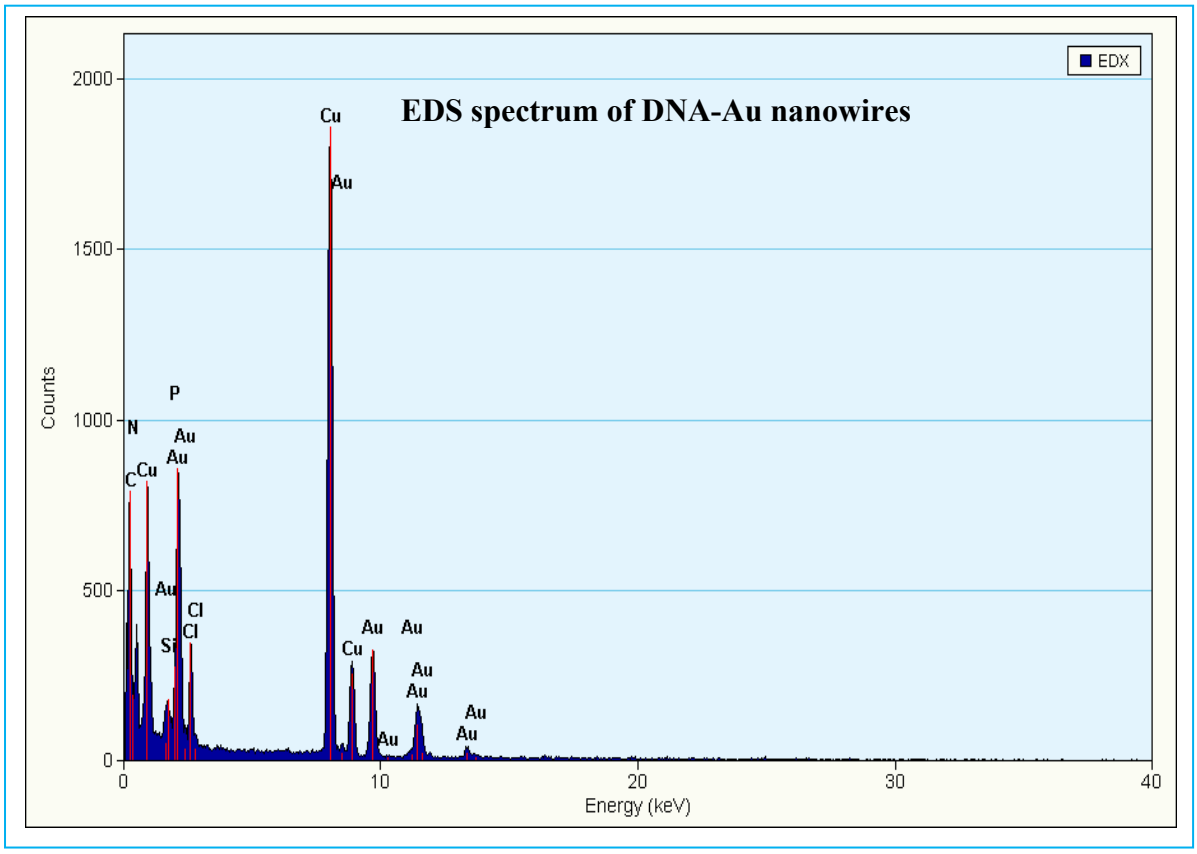

Figure S-3: The EDS spectrum of Au nanowires on DNA template. The spectrum consists of different peaks for Cu, C, Au, N, and P.

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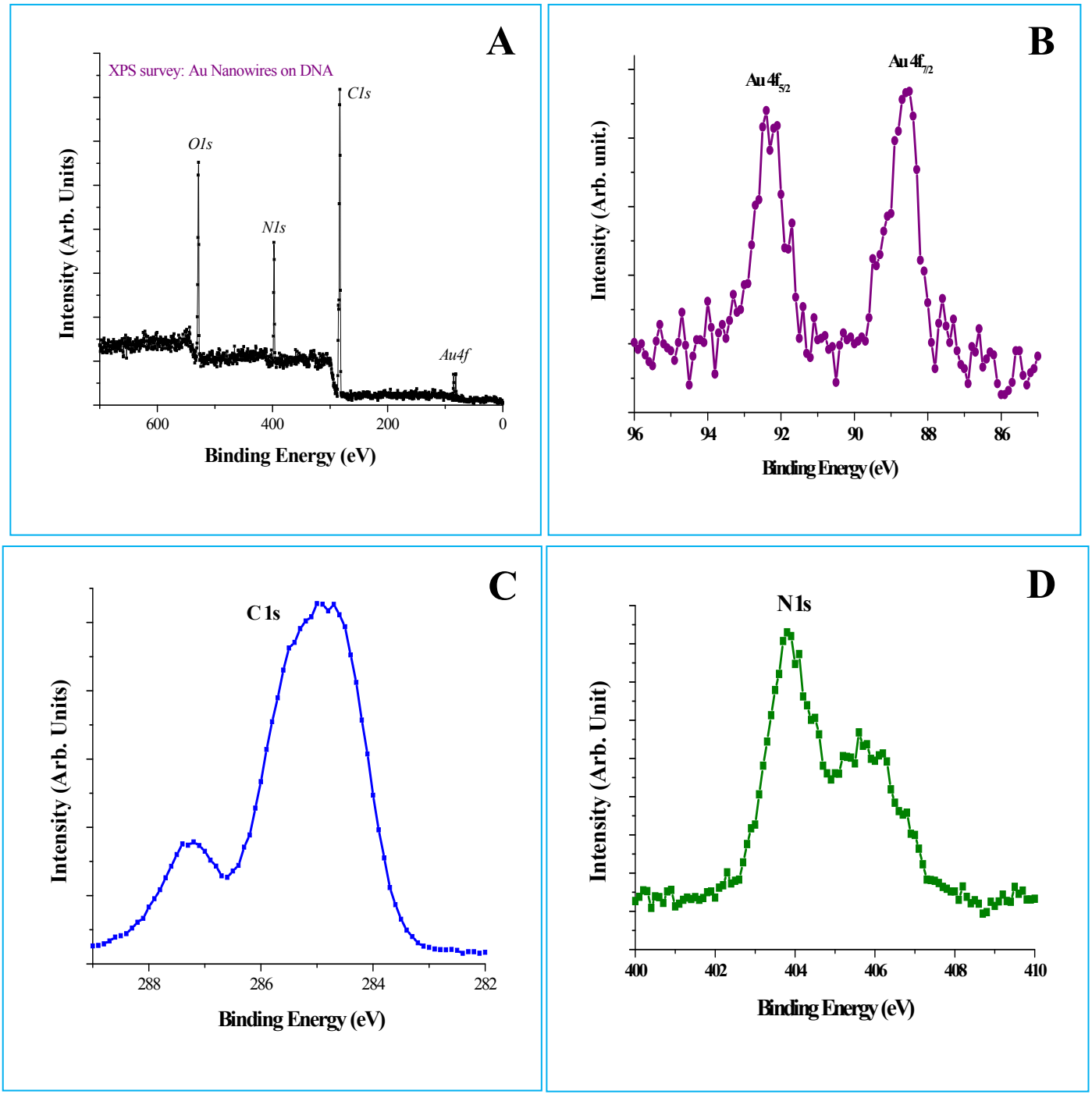

Figure S-4: The XPS spectrum DNA-Au nanowires. (A) shows the overall spectrum, (B) shows the spectrum of Au (4f) region, (C) shows the spectrum of C (1s) and (D) shows the spectrum of N (1s) respectively.

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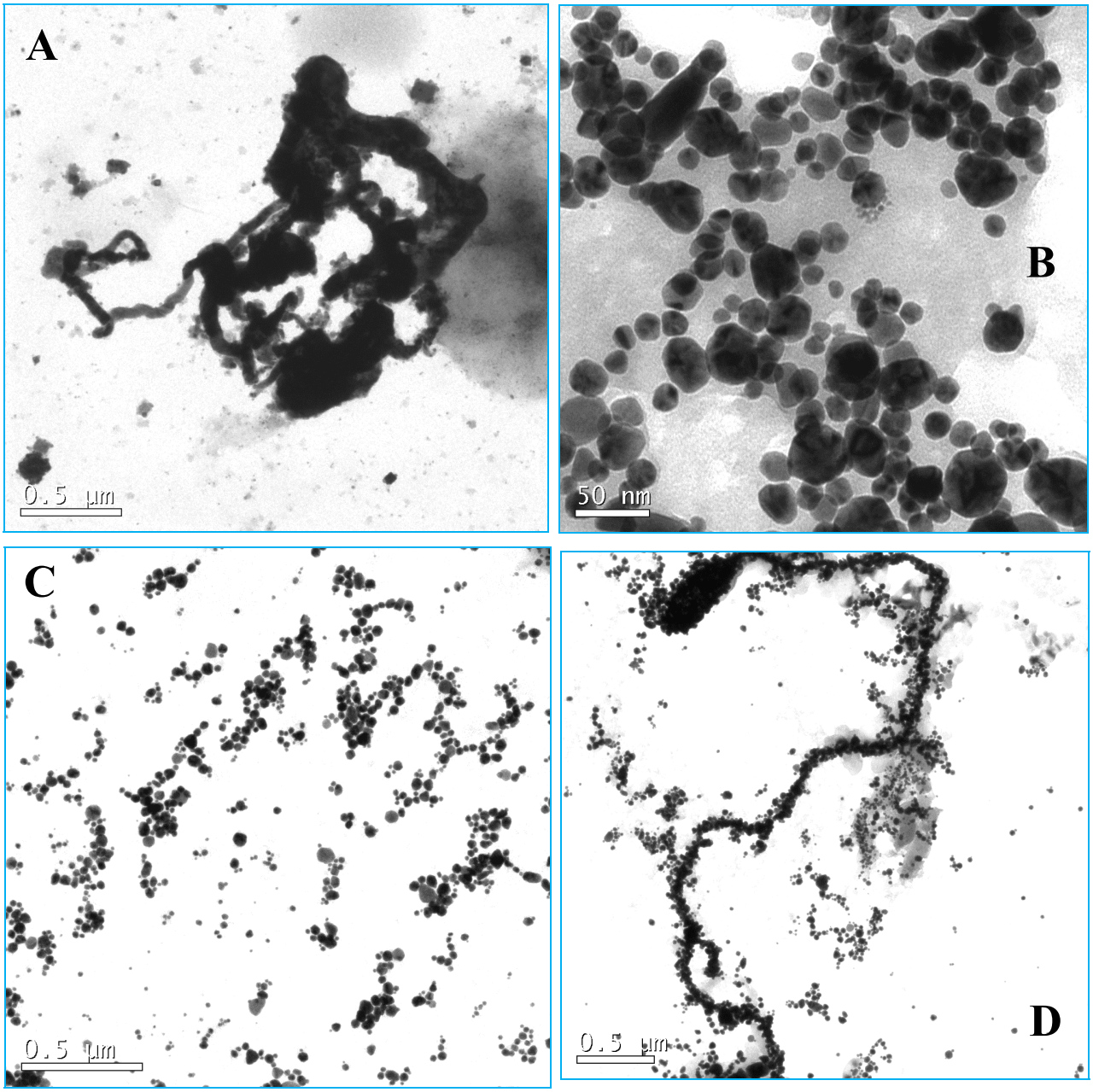

Figure S-5: TEM images at various reaction conditions. (A) shows the image at high conc. of Au(III) $\geq 10^{-1}$ M; (B) spherical Au NPs when we used free DNA bases instead of polymeric DNA; (C) branch structure Au NPs when used shorter UV irradiation (~1.5-2 hour); (D) mixture of aggregated and branch Au NPs when we expose UV light for longer period (8-10 hours).

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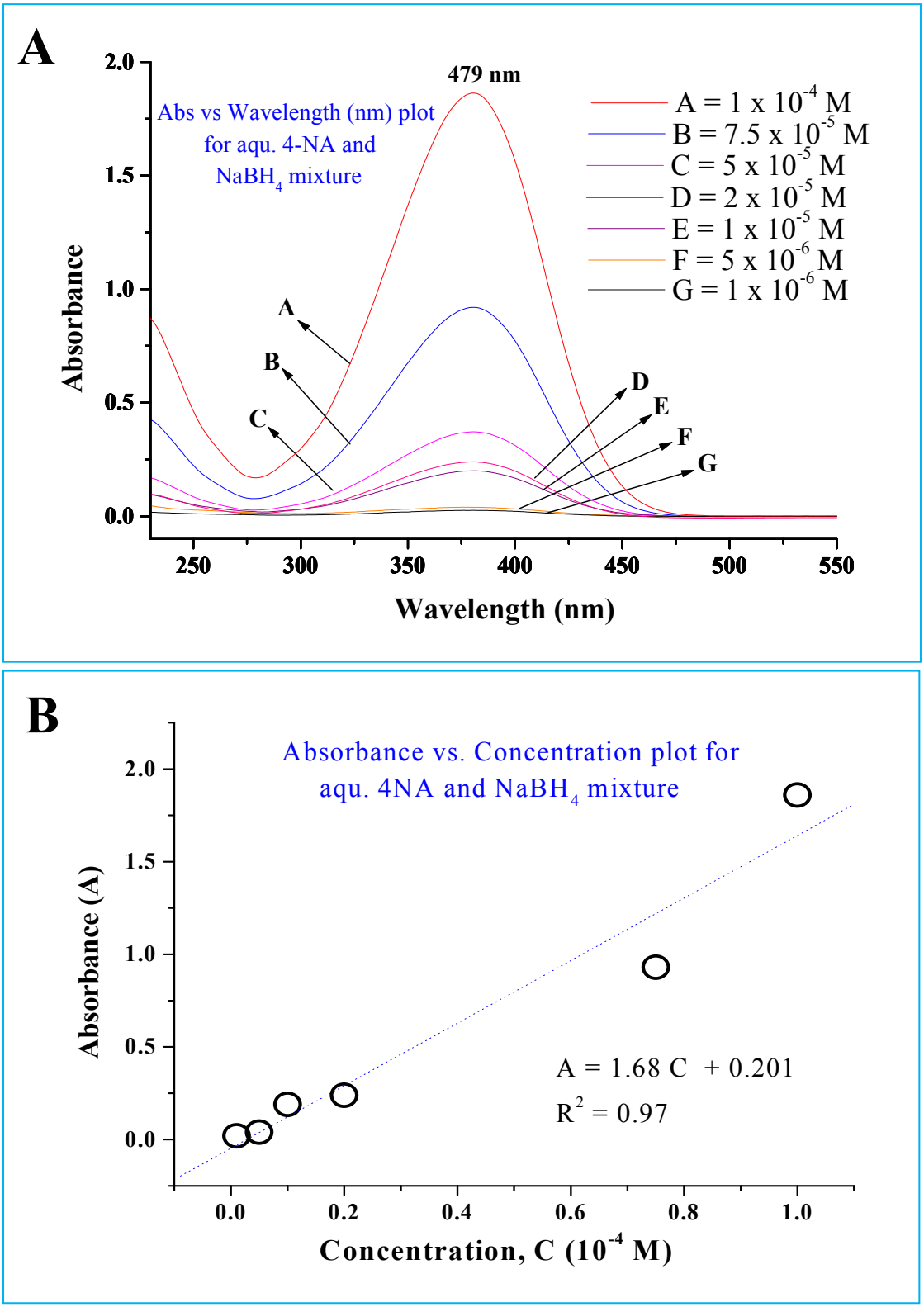

Figure S-6: Concentration dependent absorption spectra of aqueous 4-NA and $NaBH_4$ mixture (A). Calibration plot of absorbance vs concentration of of 4-NA (B).

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Table S-1: The catalytic reaction yields, TON of the catalyst per Au particles for the 4-NA catalysis reaction are summarized in Table S-1.

Name of Catalyst	**Average diameter of the individual Au NPs (nm)**	**Product yield (%)**	**Total number of Au atoms**	**TON**
Aggregated DNA-Au NPs-Set 1	~12 ± 3	~ 100	2.2×10^{13}	7.1×10^{2}
Aggregated DNA-Au NPs-Set 2	~30 ± 5	~ 100	1.44×10^{12}	1×10^{4}
Aggregated DNA-Au NPs-Set 3	~45 ± 5	~ 100	7.48×10^{11}	2.1×10^{4}