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Decoration of DNA scaffold by gold nanoparticles formed in aqueous solutions

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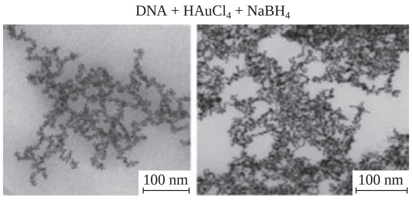
Reduction of tetrachloroaurate(III) ions in solutions of native DNA results in a formation of either small gold nanoparticles or continuous nanowires decorating DNA macromolecular template.



DNA has been recognized for its high affinity to transition metals.[1–3] This property of DNA has been utilized to template the 1-, 2- and 3-dimensional nanostructures[4–6] with potential application in nanoelectronics, catalysis, sensors production, *etc*. However, a fundamental understanding on the process of nanostructures formations on DNA template still requires in-depth investigation. In this communication we describe the influence of the DNA macromolecular template on the process of gold nanoparticles (AuNPs) formation *via* reduction with sodium borohydride and emphasize the importance of the DNA template for small AuNPs stabilization and assembly along the DNA macromolecular scaffold into necklace-like structures.

Salmon sperm DNA (300–500 bp) from MP Biomedicals Inc. was used as a template for metallization. The reduction of 3.8×10^{-4} M $HAuCl_4$ solution by $NaBH_4$ was performed in DNA solutions at the equimolar ratio between $AuCl_4^-$ anions and DNA nucleotides (3.8×10^{-4} M) in the presence of either equimolar amount or 10-fold excess of $NaBH_4$. The UV-VIS absorbance spectra of both solutions after the reaction are shown in Figure 1(*a*). The absorbance peaks at 520 nm corresponding to the characteristic surface plasmon resonance absorption of AuNPs were observed in the spectra of both samples, but the absorbance was stronger in the case of the higher $NaBH_4$ concentration. Transmission electron microscopy (TEM) images of the both samples are shown in Figure 1(*b*) and (*c*). At equimolar ratio between $HAuCl_4$ and $NaBH_4$, only a few individual AuNPs of *ca*. 3 nm size were observed on a microscopic grid. At higher concentration of $NaBH_4$, a large number of AuNPs was formed, and their ordered arrangement on a TEM grid [Figure 1(*c*)] suggests their assembly along a linear template, *i.e.* DNA macromolecules.

Since the amount of the gold precursor was the same in the both cases, the drastic increase in the number of AuNPs produced in the presence of excess of $NaBH_4$ evidenced that equimolar amount of the reducing agent with respect to the gold containing anions was not sufficient for complete reduction of all $AuCl_4^-$ anions present in the system.

In order to clarify the effect of the DNA template amount on the morphology of gold nanostructures, we performed the $HAuCl_4$ reduction in the solutions containing varied concentrations of DNA: 7.5×10^{-5}, 3.8×10^{-4}, and 1.9×10^{-3} mol dm^{-3}, the DNA : $HAuCl_4$: $NaBH_4$ molar ratio being of 1 : 1 : 10. Hence, raising the DNA concentration was accompanied by the proportional increase of $HAuCl_4$ and $NaBH_4$ concentrations in the solution. The spectra of the resulting reaction mixtures are summarized in Figure 2(*a*). The corresponding TEM images of gold nanostructures formed in those samples are shown in Figure 2(*b*)–(*d*). At the lowest DNA concentration, the characteristic plasmon resonance absorbance was weak, and the peak at *ca*. 500 nm was not pronounced. The weak plasmon absorbance coincides with the TEM images showing only a small number of AuNPs, either individual or slightly aggregated. At the higher DNA concentration (3.8×10^{-4} mol dm^{-3}), the overall absorbance of the solution over the visible spectral range increased and the absorbance peak was shifted to 520 nm and became more intense. The corre-

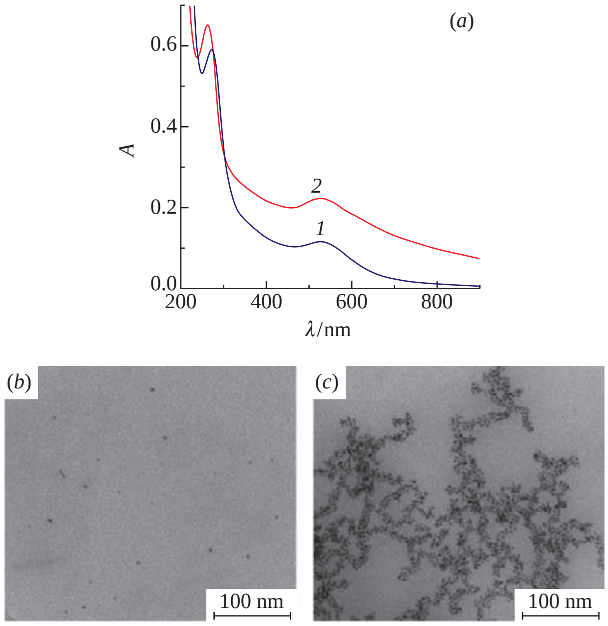


Figure 1 (*a*) UV-VIS spectra of gold nanostructures formed in DNA solution (3.8×10^{-4} mol dm^{-3}) containing equimolar amount of $HAuCl_4$ and (*1*) ×1 or (*2*) ×10 amount of $NaBH_4$. TEM images of nanostructures formed in the above solutions with (*b*) ×1 and (*c*) ×10 amount of $NaBH_4$.

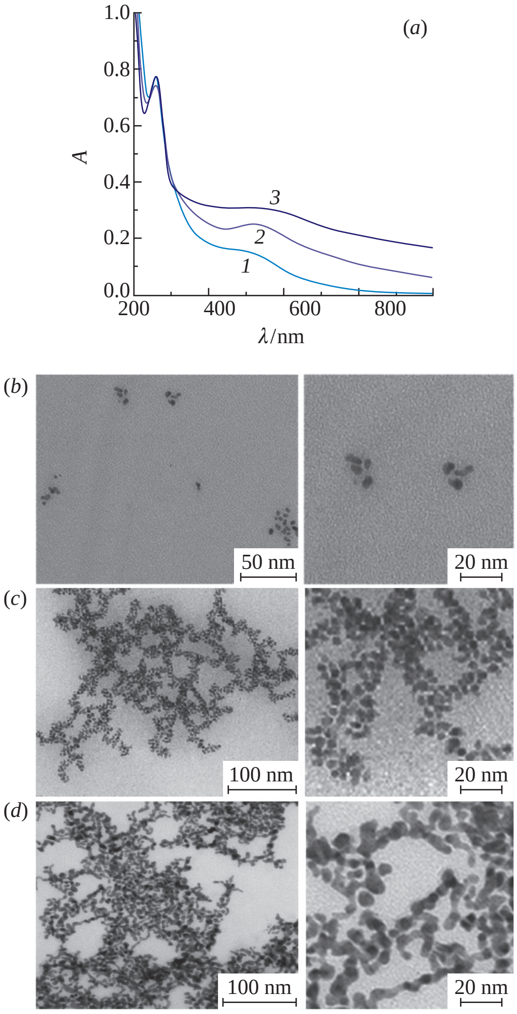


Figure 2 (*a*) UV-VIS spectra of gold nanostructures formed in DNA solutions of concentrations (*1*) 7.5×10^{-5}, (*2*) 3.8×10^{-4}, and (*3*) 1.9×10^{-3} mol dm^{-3} containing equimolar amount of $HAuCl_4$ and 10-fold excess of $NaBH_4$ (the solutions were diluted to the same DNA concentration prior to the measurement). TEM images of nanostructures formed in the solutions of (*b*) 7.5×10^{-5}, (*c*) 3.8×10^{-4}, and (*d*) 1.9×10^{-3} mol dm^{-3} DNA concentration.

sponding TEM images reveal the formation of necklace-like structures composed of numerous 2–3 nm AuNPs [Figure 2(*c*)]. In the necklace-like nanostructures, AuNPs grown on DNA are clearly separated and show no aggregation or fusion. Finally, at the highest DNA concentration (1.9×10^{-3} mol dm^{-3}), the solution absorbance increased further [Figure 2(*a*)], especially at $\lambda > 600$ nm, corresponding to a collective particle surface plasmon effect.[7] The growth and shift of absorbance to longer wavelengths indicates that particles are partially aggregated into continuous wire-like gold nanostructures which might be ascribed to the high concentration of $HAuCl_4$. In wire-like nanostructure no discrete AuNP can be identified.

Note that owing also to the templating effect of the macromolecule the AuNPs prepared in the presence of DNA appeared to be non-spherical in the TEM images.

The observed drastic morphological changes of metal nanostructures formed at high DNA concentration suggest a change in the mechanism of the AuNPs growth. Very similar change from a nucleation–growth pathway to a nucleation–aggregation–smoothing pathway has been described earlier,[8] where elongated wire-like Au nanostructures have exhibited the intermediate morphology formed *via* aggregation and fusion of rapidly formed AuNPs. Such elongated aggregates have been finally transformed into larger AuNPs. In the same manner, small AuNP nuclei that were formed in the DNA solution at high concentrations of $HAuCl_4$ and $NaBH_4$ aggregated onto the DNA chain and grew to continuous metal nanowires. Importantly, in contrast to the DNA-free system described in ref. 8, elongated Au nanostructures were stabilized by DNA template, and Au nanowires could be obtained in a high yield.

In conclusion, we have demonstrated that DNA serves as a macromolecular template in the course of $HAuCl_4$ reduction in aqueous solutions, affording the one-dimensional AuNP nanostructures with DNA being decorated either by small 3 nm AuNPs or by continuous gold nanowires. The formation of different one-dimensional assemblies strongly depends on the concentration of DNA and other chemicals used for DNA metallization.

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