Electronic supplementary information

A high local DNA concentration for nucleating a DNA/Fe coordination shell on gold nanoparticles

Zhicheng Huang [a] , Biwu Liu [a] and Juewen Liu [a]*

Department of Chemistry, Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada.

E-mail: liujw@uwaterloo.ca

Materials and Methods

Chemicals. The thiolated DNA (5'-TCACAGATGCGTAAAAA-SH-3') was purchased from Integrated DNA Technologies (IDT, Coralville, IA). $FeCl_2 \cdot 4H_2O$ was purchased from Alpha Aesar. Ethylenediaminetetraacetic acid (EDTA), sodium phosphate monobasic, doxorubicin hydrochloride (DOX), $HAuCl_4$, and KCN were purchased from Sigma-Aldrich. AuNPs (13 nm diameter) were synthesized following the procedure in the literature.[1] Based on an extinction coefficient of 2.7×10^8 liter $mol^{-1} \cdot cm^{-1}$ at $\lambda = 520$ nm for 13 nm AuNP, the stock concentration of 13 nm AuNP was 9.67 nM.[2]

AuNP@DNA preparation. The thiolated DNA (final concentration 4 μM) was mixed with the AuNP solution (9.67 nM) and incubated under room temperature for 1 h. Then, the DNA-AuNP mixture was incubated in a -20 °C refrigerator for 12 h to freeze. No salt or additional buffer was added for attaching the DNA onto the AuNPs by the freezing method.[3] The obtained conjugate was named AuNP@DNA. For most experiments, the free DNA strands that were not attached were not removed. In some control experiments, to remove the free DNA, the frozen sample was thawed at room temperature and centrifuged at 10000 rpm for 10 min. The supernatant was removed and the pallet was re-dispersed in the same volume of Milli-Q water.

AuNP@DNA/Fe preparation. The above prepared AuNP@DNA was used. A Fe^{2+} solution was prepared freshly with Milli-Q water at a concentration of 100 mM. To avoid the oxidation of Fe^{2+}, the Milli-Q water was treated with N_2 gas. In a typical experiment, 1 mL AuNP@DNA was added into 9 mL H_2O in a round-bottom flask. Then, concentrated Fe^{2+} (100 mM) was added to a final concentration of 1 mM into the mixture under stirring. After this, the mixture was heated to 95°C for 3 h. For AuNP@DNA/Fe formed with different DNA concentrations, PCR tubes were used for the reactions with a total volume of 100 μL and the temperature was controlled using a PCR thermocycler. In all these reactions, the final AuNP concentration was 1 nM during the heating process.

DOX adsorption and release. Before mixed with DOX, all nanoparticles were washed with water by centrifugation. To load DOX, 1 μM DOX was mixed with 0.2 nM AuNPs with a total volume of 500 μL in water and incubated at room temperature for 4 h. The adsorption capacity of DOX was determined by the fluorescent intensity of the free DOX remained in the supernatant. For DOX release, AuNP@DNA/Fe/DOX was incubated with 1× PBS. Fluorescent spectra were measured before and after 4 h incubation with excitation at 500 nm.

Methods for TEM. TEM images were taken by a Phillips CM10 100 kV transmission electron microscope. All the samples were washed with Milli-Q water before preparing TEM samples.

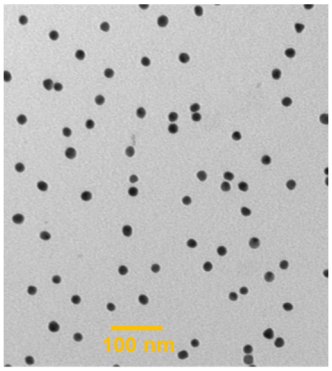

Fig S1. A TEM image of the AuNP@DNA with the existence of excess free DNA incubated under 95°C for 3 h without Fe^{2+}.

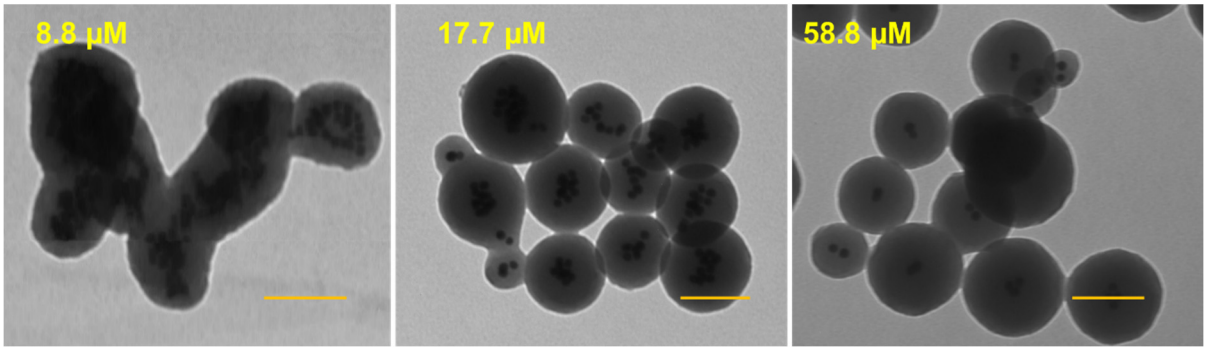

Fig S2. TEM micrographs of AuNP@DNA/Fe formed with various DNA concentrations. In all samples, 1 mM Fe^{2+} was used. In these TEM images, the number of AuNPs in each sphere decreased as the DNA concentration increased. Scale bars: 100 nm.

References

[1] J. Liu, Y. Lu, *Nat. Protoc.* **2006**, *1*, 246.
[2] H. D. Hill, C. A. Mirkin, *Nat. Protoc.* **2006**, *1*, 324-336.
[3] B. Liu, J. Liu, *J. Am. Chem. Soc.* **2017**, *139*, 9471-9474.