Electronic Supplementary Information

Core solution: a strategy towards gold core/non-gold shell nanoparticles bearing strict DNA-valences for programmable nanoassembly

Huiqiao Wang, a Yulin Li, a Ming Gong, b and Zhaoxiang Deng*, a

a CAS Key Laboratory of Soft Matter Chemistry & Collaborative Innovation Center of Suzhou Nano Science and Technology, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China. E-mail: zhxdeng@ustc.edu.cn

b Engineering and Materials Science Experiment Center, University of Science and Technology of China, Hefei, Anhui 230027, China
Experimental details

DNA sequences: DNA oligonucleotides were custom-synthesized by Sangon Bioengineering Technology and Services Co., Ltd. (Shanghai, China) and purified by PAGE (unmodified DNA) or HPLC (thiolated DNA). All DNA oligos were subject to a molecular weight verification by MALDI-TOF mass spectroscopy. Following are the sequences (5’-3’) of the DNA oligonucleotides used in this work. Italic bases showed the complementary parts between ssDNA and ssDNAc.

**dT10** strand (10 bases):

HS-5’TTTTTTTTTT3’

**ssDNA** (89 bases):

HS-5’GCAGTAACGCTATGTGACCGAGAAGGATTCGCATTTGTAATCTTTGAGCCCGCACGAAACCTGGACACCCCTAAGCAACTCCGTATCAGA3’

**ssDNAc** (89 bases):

HS-5’GCAGTAACGCTATGTGACCGAGAAGGATTCGCATTTGTAATCTTTGAGCCCGCACGAAACCTGGACACCCCTAAGCAACTCCGTATCAGA3’

**SuperDNA-1** (55 bases):

HS-5’TTACTGACATGAAGCCGGATATAGATTCTGGAGCGATCGTCCTCCTTGAAGCTAG3’

**SuperDNA-1c** (55 bases):

HS-5’GCAGTAACGCTATGTGACCGAGAAGGATTCGCATTTGTAATCTTTGAGCCCGCACGAAACCTGGACACCCCTAAGCAACTCCGTATCAGA3’

**SuperDNA-2** (59 bases):

5’GCCTGCGTAATGCCGTACTTAATGCTATCTCGAGAGTCAGTCCCTAGCTTCAAGGAGGA3’

**SuperDNA-3** (59 bases):

5’ACGGCATTACGCAGGCCCTGCAGTTCCGTCATTATCTCTAGCTTCAAGGAGGA3’

Chemicals: ascorbic acid (AA) and AgNO₃ were obtained from Bio Basic Inc. (BBI, Canada); NaBH₄ was from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China); polyvinylpyrrolidone (PVP K40, MW= 40 000), sodium citrate tribasic dihydrate and Na₂PdCl₄ were purchased from Sigma; bis(p-sulfonatophenyl) phenylphosphine dihydrate dipotassium salt (BSPP) was a product of Strem Chemical (Newburyport, MA, USA). All the reagents were used as received without further purification.


AgNPs: Citrate-protected silver nanoparticles were prepared by injecting 100 μL of 100 mM NaBH₄ to an aqueous solution containing 0.1 mM AgNO₃ and 1 mM trisodium citrate (or 0.2 % PVP for PVP protected AgNPs) under vigorous stirring. The reactions lasted for 30 minutes at room temperature.

Au@AgNPs with a dT₁₀ DNA modified inner gold core: Firstly, 5’-thiolated dT₁₀ strand was combined with 1 μM AuNPs with a diameter of 5 nm at a 20:1 molar ratio and incubated in a 0.5×TBE (Tris, 44.5 mM; EDTA, 1 mM; boric acid, 44.5 mM; pH 8.0) buffer in the presence of 100 mM NaCl for 4 hours at 20 °C. After removing excess dT₁₀ DNA by centrifugation, 40 μL of the dT₁₀-modified AuNPs at a concentration of 1 μM was mixed with 8 μL 45 mM AgNO₃, 8 μL 100 mM ascorbic acid, and 2 μL 5% PVP in 0.5×TBE plus 0.1 M
NaCl. The reaction lasted for 2 h at room temperature.

Discrete DNA conjugation of dT10-stabilized Au@AgNPs: 5'-thiolated ssDNA or ssDNAc strand was added to a solution containing as-prepared Au@AgNPs at an appropriate molar ratio. NaCl or NaAc was added to reach a final concentration of 100-500 mM. The resulting solution was incubated at 20 °C for 10 hours. The ssDNA or ssDNAc conjugated product was loaded in a 3% agarose gel, and run in 0.5×TBE at 13 V/cm for an electrophoretic separation.

PdNPs: 10 μL of 0.1 M Na2PdCl4 and 10 μL of 25 mM sodium citrate were added to 1 mL doubly distilled H2O (ddH2O) under vigorous stirring. Freshly prepared 30 μL of 0.1 M NaBH4 was added dropwise to the above solution, which caused an instant color change. The mixture was stirred for an additional 30 min at room temperature before use.

Au@PdNPs: The synthesis of Au@PdNPs was based on previous publications (Lu, L. H.; Wang, H. S.; Xi, S. Q.; Zhang, H. J. J. Mater. Chem. 2002, 12, 156-158; Hu, J. W.; Zhang, Y.; Li, J. F.; Liu, Z.; Ren, B.; Sun, S. G.; Tian, Z. Q.; Lian, T. Chem. Phys. Lett. 2005, 408, 354-359) Briefly, a 380 μL solution containing 1 mM Na2PdCl4, 50 nM AuNPs, and 1 mM sodium citrate was chilled in an ice-water bath. Next, 20 μL of 50 mM ice-cooled ascorbic acid was added dropwise to the above solution under continuous stirring. The reaction mixture turned dark brown within minutes. After a 45 min reaction, 8 μL of 50 mg/mL BSPP was introduced to initiate a ligand-exchange of the citrate ligands on the Au@PdNPs. After 5 hours, the solution was centrifuged at 16200 g for 30 min and the Au@PdNP precipitates were redispersed in ddH2O. Owing to the highly selective Pd deposition on the AuNPs, the concentration of as-obtained Au@PdNPs could be estimated from the initial concentration of the AuNPs.

Superstructured DNA ligand: Three component strands including SuperDNA-1, 2, and 3 were stoichiometrically mixed in 0.5×TBE containing 50 mM NaCl. The solution was thermally annealed to form a superstructured DNA (see Figure S7) following a temperature program: 95°C for 3 min, 65°C 5 min, 50°C 10 min, 37°C 10 min, and room temperature 15 min.

Discrete DNA conjugation of AuNPs and Au@PdNPs: Thiostated DNA single strand (i.e. ssDNA, ssDNAc, or SuperDNA-1c) or a DNA superstructure ligand (formed by SuperDNA-1, 2 and 3) were combined with AuNPs or Au@PdNPs at appropriate molar ratios in 0.5×TBE containing 100 mM NaCl. The conjugation reaction took place at 20 °C for 3 hours. The product was loaded in a 3% agarose gel, and run at 13 V/cm in 0.5×TBE at room temperature to achieve an electrophoretic valence separation.

High density DNA modification of Au@PdNPs: 5'-thiolated ssDNA was combined with Au@PdNPs at 80:1 molar ratio with a final concentration of 100 nM for the Au@PdNPs. NaCl was gradually introduced over 48 h to reach a final concentration of 300 mM. The solution was centrifuged twice at 16200 g for 30 min to remove unbound DNA, and the precipitates of nanoparticles were redispersed in 0.5×TBE plus 100 mM NaCl.

DNA-programmed nanoparticle assembly: As-obtained DNA conjugates of AuNPs, Au@AgNPs, or
Au@PdNPs were mixed at appropriate stoichiometry and incubated in 0.5×TBE plus 125 mM Na\(^+\) for 20 h. 3% (2% for the core-satellite structures) agarose gel electrophoresis was used for the characterization and isolation of assembled products.

**Spectroscopic and TEM characterizations:** UV-vis absorbance data were recorded by a Hitachi U-2910 spectrophotometer. Transmission electron microscope (TEM) imaging was conducted on a JEM-2100F field emission transmission electron microscope operated at an acceleration voltage of 200 kV. Samples were deposited on a carbon coated copper grid for TEM analysis.
Figure S1. Pd and Ag nanoparticles synthesized in the absence of gold nanoparticle seeds. PdNPs (a) and AgNPs (b) were synthesized with NaBH₄ as a reductant and citrate as a stabilizer; AgNPs (c) were synthesized by reducing AgNO₃ in the presence of PVP stabilizer. It was hard to achieve uniform products for both PdNPs (a) and AgNPs (b,c) under these conditions via a seed-free process.
**Figure S2.** Gel electropherograms showing that the DNA conjugation of Au@AgNPs could be further improved by increasing the Na\(^+\) concentration. The left gel corresponded to DNA conjugation reactions carried out in 0.1 M NaAc, and the right gel corresponded to 0.5 M NaAc.

![Gel electropherograms showing DNA conjugation of Au@AgNPs](image)
Figure S3. TEM images of Au@AgNP dimers stored at 4°C for different periods, verifying a high stability of the dimer structures.
Figure S3. (Continued)

Two weeks

Three weeks
Figure S3. (Continued)
**Figure S4.** Statistical histograms showed that the measured interparticle gaps (the margin part between two particles, not including the particle radii) widely ranged from 2.1 nm to 29 nm ($N = 141$) for the Au@AgNP dimers (Figure 3f), and 1.2 nm to 30.5 nm ($N = 161$) for the AuNP dimers (Figure 3e), respectively. As expected, the observed distances were shorter than the total length of the DNA linker (17 nm for the 50-bp duplex part plus two 39-base flanking single stranded segments). The results were reasonable for tethered nanodimers considering the high flexibility of the DNA linkers (especially the single stranded parts). Meanwhile, the existence of interparticle lateral capillary force during sample drying on a TEM carbon film could also bring two objects closer.
Figure S5. HAADF STEM (high angle annular dark field scanning transmission electron microscopy) images of Au@Ag core-shell nanoparticles and corresponding EDS (energy-dispersive X-ray spectroscopic) elemental mapping. Red and green pixels were Lα signals from Au and Ag elements, respectively.
Figure S6. Salt stability test of BSPP-capped Au@PdNPs. The samples were challenged by different concentrations of NaCl and then stored at room temperature for 24 hours. As shown below, the Au@PdNPs was very stable in 0.1 M NaCl, while 0.2 M NaCl would cause a precipitation of the sample. These results were consistent with the gel electrophoresis data in Figure 4b.

\[ \text{[NaCl]:} \quad 0.0 \text{ M} \quad 0.1 \text{ M} \quad 0.2 \text{ M} \]
**Figure S7.** Schematic representation of a DNA superstructure (formed by SuperDNA-1, 2, and 3) conjugated Au@PdNP and its hybridization with a SuperDNA-1c conjugated AuNP to form Au@PdNP-AuNP heterostructures.
**Figure S8.** Statistical analysis of the assembly yields for Au@PdNP-AuNP heterostructures. Panels (a)-(d) corresponded to the products in Figure 4 (g)-(h). The histograms were based on a total number of particles of 386, 313, 477 and 750 for (a)-(d), respectively. Asterisks marked desired products. The assembly yields were lower than the Au@Ag and AuNP homo-assemblies (see Figure 3d in the main text) but higher than previously reported Au-Pt heterostructures (Chem. Commun. 2012, 48, 3727-3729).
Figure S9. Core-satellite assemblies formed between Au@PdNPs and AuNPs. (a) 2% agarose gel electrophoresis showing the hybridization (lane 2) between ssDNA-multifunctionalized Au@PdNPs (lane 1) and ssDNAc-monofunctionalized 5 nm AuNPs (lane 3). AuNPs were added in slight excess to ensure an efficient utilization of the core particles. (b) TEM images of as-assembled core-satellite superstructures. Ungrouped nanoparticles were negligible on the TEM image, evidencing a strong DNA bonding on the Au@PdNPs.
Figure S10-1. Surface enhanced Raman scattering (SERS) of surface adsorbed 4-Mercaptopyridine (4-Mpy) on Au@Ag core-shell nanoparticles, excited by (a) a 532 nm and (b) a 670 nm laser, respectively. Inset in (a) was a TEM image of as-synthesized Au@Ag nanoparticles with a thickened silver shell (Nam et al. J. Am. Chem. Soc. 2012, 134, 5456–5459) to achieve an efficient Raman enhancement. As low as $5 \times 10^{-8}$ M 4-Mpy could be detected (see marked scattering peaks in (b)).
Figure S10-2. Surface enhanced Raman scattering (SERS) of surface adsorbed 4-Mercaptopyridine (4-Mpy) on Ag nanoparticles (see Figure S1(b)), excited by (a) a 532 nm and (b) a 670 nm laser, respectively. As low as $5 \times 10^{-7}$ M 4-Mpy could be detected (see marked scattering peaks).
Figure S10-3. Raman scattering data of 4-Mercaptopyridine (4-Mpy) aqueous solutions in the absence of a SERS substrate, excited by (a) a 532 nm and (b) a 670 nm laser, respectively. These curves lacked any Raman signals from 4-Mpy due to the very low scattering probability.
Figure S11. Au@PdNP (0.5 nM) catalyzed hydrogenation of 4-nitrophenol (4-NP) (60 μM) into 4-aminophenol (4-AP) by reduction with NaBH₄ (2.5 mM). Note that Au@PdNPs showed good catalytic activities (b, c) slightly lower than pure PdNPs (d), in contrast to the core AuNPs (a) for which no significant catalysis happened. The PdNPs showed a better activity presumably due to its smaller size (see Figure S1 (a)) and thus a higher total surface area (the same masses of Pd were used in (b-d)).
Figure S12. Gel electrophoresis showed that the original DNA valences on an AuNP core would be partially deteriorated after a silver deposition. Lane 1: dT$_{10}$ coated 5 nm AuNPs; lane 2: 89-base ssDNA decorated dT$_{10}$-AuNP conjugates; lanes 3-4 corresponded to the samples in lane 2 and lane 1 after silver depositions, respectively. The samples were run in a 3% agarose gel at 13 V/cm. Note that the gel band in lane 3 was very close to lane 4 where the ssDNA was absent from the Au core.
**Figure S13.** Gel electrophoresis of DNA functionalized PdNPs and AgNPs synthesized in the absence of gold cores. Lanes 1 to 3 corresponded to increased ratios of thiolated ssDNA. PdNPs did not appear as a sharp band, and AgNPs were not able to move into a gel. DNA valences for both particles were not resolvable. These data further evidenced the pivotal role of a gold core inside the core-shell nanoparticle for a gel electrophoretic DNA-valence separation.