Core-Shell Assisted Bimetallic Assembly of Pt and Ru Nanoparticles by DNA Hybridization

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***Abstract* – We have discovered that the current protocols to assemble Au nanoparticles based on DNA hybridization do not work well with the small metal nanoparticles (e.g. 5 nm Au, 3.6 nm Pt and 3.2 nm Ru particles). Further investigations revealed the presence of strong interaction between the oligonucleotide backbone and the surface of the small metal nanoparticles. The oligonucleotides in this case are recumbent on the particle surface and are therefore not optimally oriented for hybridization. The nonspecific adsorption of oligonucleotides on small metal nanoparticles must be overcome before DNA hybridization can be accepted as a general assembly method. Two methods have been suggested as possible solutions to this problem. One is based on the use of stabilizer molecules which compete with the oligonucleotides for adsorption on the metal nanoparticle surface. Unfortunately, the reported success of this approach in small Au nanoparticles (using K_2BSPP) and Au films (using 6-mercapto-1-hexanol) could not be extended to the assembly of Pt and Ru nanoparticles by DNA hybridization. The second approach is to simply use larger metal particles. Indeed most reports on the DNA hybridization induced assembly of Au nanoparticles have made use of relatively large particles (>10 nm), hinting at a weaker non-specific interaction between the oligonucleotides and large Au nanoparticles. However, most current methods of nanoparticle synthesis are optimized to produce metal nanoparticles only within a narrow size range. We find that core-shell nanoparticles formed by the seeded growth method may be used to artificially enlarge the size of the metal particles to reduce the nonspecific binding of oligonucleotides. We demonstrate herein a core-shell assisted growth method to assemble Pt and Ru nanoparticles by DNA hybridization. This method involves firstly synthesizing approximately 16 nm core-shell Ag-Pt and 21 nm core-shell Au-Ru nanoparticles from 9.6 nm Ag seeds and 17.2 nm Au seeds respectively by the seed-mediated growth method. The core-shell nanoparticles were then functionalized by complementary thiolated oligonucleotides followed by aging in 0.2 M PBS buffer for 6 hours. The DNA hybridization induced bimetallic assembly of Pt and Ru nanoparticles could then be carried out in 0.3 M PBS buffer for 10 hours.**