이 학 석 사 학 위 논 문

Synthesis and Optical Properties of DNA Modified Au–Au Nanosnowmen with ~1nm Nanogap

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2018년 8월

서울대학교 대학원

화학부 무기화학 전공

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Synthesis and Optical Properties of DNA Modified Au–Au Nanosnowmen with ~1nm Nanogap

By

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Department of Chemistry

Graduate School

Seoul National University

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차영석의 석사학위 논문을 인준함

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위 원 장 이 동 환 (인)

부 위 원 장 남 좌 민 (인)

위 원 김 지 환 (인)

Abstract

Synthesis and Optical Properties of DNA Modified Au-Au Nanosnowmen with ~1nm Nanogap

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To detect a wide variety of target materials, particularly biomaterials with high sensitivity, it is a very promising technology to use nanoprobes that emit strong optical signals. Most important in this detection method is the presence of nanoprobes that generate consistent strong optical signals, and therefore it is very important to synthesize these nanoprobes at high yields. Localized Surface Plasmon Resonance (LSPR), a typical property of metal nanoparticles, allows the metal nanoprobe to emit strongly amplified fluorescence or SERS signals. In particularly, when metal nanoprobes have nano-sized crevices or nano-sized gaps, plasmonic coupling occurs at very short distances. Thus, in

Nanocrevice and Nanogap, the strength of the electromagnetic field is strongly amplified. When a substance that emits an optical signal located in a strongly amplified electric field, it emits a strongly amplified optical signal. This paper also discusses the optical properties of Au-Au nanosnowmen structures and discusses the stability of optical signals in a living environment that is required for future bioapplication.

Keyword : Plasmonics, Nanoprobe, Plasmonic coupling, Localized Surface Plamson Resonance(LSPR), Surface Enhanced Raman Scattering(SERS), DNA Sequence

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1. Introduction

Plasmonics is a discipline that exploits the properties of metallic nanometer-sized metal particles interacting with light. Metal nanoparticles of various types and shapes interact with light of a specific wavelength in various ways. While these properties of metal nanoparticles are worthy of their own investigation, they can be useful in many fields. It can be used as a tool to facilitate research, especially in medical and biological field, or it can be used for treating patients.

Localized Surface Plasmon Resonance (LSPR) is a phenomenon that occurs when the wavelength of light applied is larger than the size of metal nanoparticles, which means that the electron cloud of metal nanoparticles is affected by the electromagnetic field and causes collective oscillation to generate resonance. [1-4]

The LSPR is influenced by the size, shape, constituent elements of the metal nanoparticles, distance between the metal nanoparticles and the solvent. To control plasmonic properties, recent nanotechnologies have sophisticatedly studied to control the structure of plasmonic nanoparticles. [1-7]

It is also important to precisely synthesize the structure of the metal nanoparticles by controlling the structure itself, but assembly is also one of the methods. This is possible by surface modification

of the appropriate ligand. The most common ligand for assembling metal nanoparticles is DNA. Single strand DNA combines with another single strand DNA having a complementary base sequence to form a double helix structure. Through this principle, metal nanoparticles can be coupled. After each single strand DNA (ssDNA) is bound to metal nanoparticles, the metal nanoparticles can be assembled by complementary binding of the DNA. By adjusting the distance between the metal nanoparticles, the plasmonic properties can be changed and the intensity of the optical signal can be amplified. [8-13]

These properties make them available for bio-sensing applications. In addition to the property of complementary binding, DNA is easier to bioapplication because it is easy to modify sequence, length, Raman dye and fluorescent dye.

When plasmonic coupling occurs between metal nanoparticles, the intensity of the electromagnetic field (EM field) around it increases, so the intensity of the Raman signal or fluorescence in the region increases. As the distance between particles decreases, a longitudinal mode of plasmon mode is observed and plasmonic coupling occurs more and more strongly. The phenomenon is maintained until the distance between particles is 0.5 nm, and as the distance further decreases, the quantum effect occurs and the plasmonic coupling disappears. [14-17]

For a variety of bioapplications, it is common practice to use a SERS signal by placing a Raman dye on a plasmonic hot spot. Here, the hot spot means that the intensity of the EM field is greatly amplified. In general, metal nanoparticles or surface morphologies appear in a rough region. It is known that the EM field has a large value when the distance from the metal surface is close or the shape is sharp. [18-20]

In the Mirkin group, the DNA with Raman dye was coated with gold nanoparticles and then covered with a shell to obtain a strong SERS signal. In this method, the limit of detection value was about 1 fM. [21]

The SERS signal is particularly strongly amplified when the Raman dye is located in the nano-gap between the nanoparticles. Therefore, it is very important to control the distance between these particles uniformly at a high yield. In order to generate a large number of nanogaps, a half-complementary DNA sequence is attached to AgNPs attached with raman dye-attached DNA, and the particles are assembled together to form a plasmonic hot spot and show strong SERS signal intensity.[22]

To uniformly control intergranular nano-gaps, Nam and coworkers synthesized a SERS-active dimeric gold-sliver core-shell nanodumbbell. In this structure, DNA with modified raman dye was attached to gold nanoparticles, complementary DNA was

inserted, and silver shells were stacked to control the spacing between particles. In particular, by controlling the density of DNA, only two particles are allowed to bind together. [23]

However, not all the nanogaps were uniformly formed, and the nanogaps were formed in different ways because the particles tend to fall off from each other.

In the end, Nam and coworkers synthesized Au nanoparticle nanogap particles (AuNNP) with nano-gaps inside. This structure has an interior gap of about 1 nm and shows a high yield of over 90%. [24]

The structures with various nanogaps that can be the plasmonic hot spots discussed above are shown in Figure 1.

In this paper, we will synthesize another SERS nanoprobe that is different from AuNNP starting from DNA modified AuNP and look at its optical properties. This nanoprobe is an Au-Au nanosnomen and will have signal robustness that has a stronger SERS signal than AuNNP, while the Raman dye is not easily damaged by the surrounding environment. We will now look at Au-Au nanosnowmen in detail.

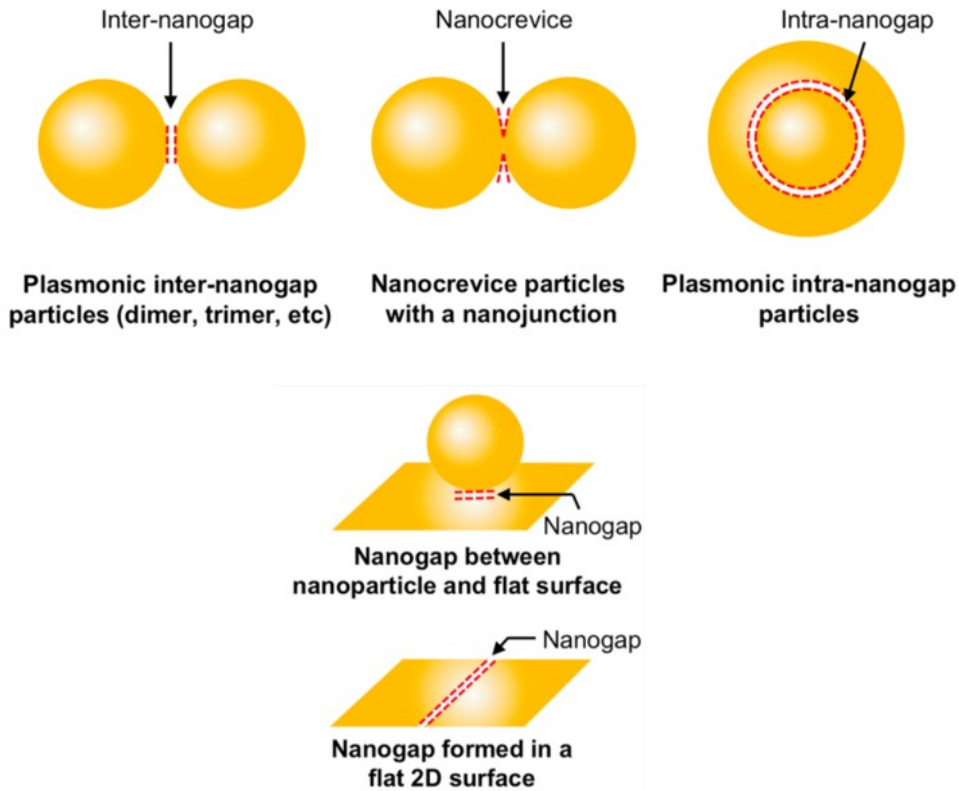

Figure 1-1. Plasmonically Coupled Nanostructures with a Nanogap.[25]

2. Experimental Session

1. Preparation of DNA-modified AuNPs

The modification of DNA on AuNPs was based on literature procedures.1-4 Oligonucleotides were reduced by dithiothreitol (DTT, 0.1 M) in phosphate-buffered saline solution (0.17 M, pH = 8.0) and then purified using a desalting NAP-5 column. For the preparation of DNA-modified AuNPs, purified DNA [5'-A20-(Raman dye)-(CH2)3-SH-3'] were used to conjugate on AuNPs. The loading number of DNA was determined based on the fluorescence analysis. DNA-modified AuNPs were mixed with 0.1M DTT for 3hrs. The loading numbers of DNA per particle were determined to be ~400strands for 40nm AuNPs. The excess amount of DNA (50 fold for Cy3) were added for DNA-modification process. Briefly, for Raman dye-modified DNA, 387 μL of 44.9 μM DNA solution was mixed in 4.5 ml of 0.1 nM 40-nm AuNP solution. The mixture was adjusted to obtain a final phosphate concentration of 10 mM (pH 7.4) with 100 mM phosphate buffer. The resulting solution was wrapped in an aluminum foil and placed on an orbital shaker at room temperature for 30 min. Next, the resulting solution was adjusted to 0.3 M NaCl (0.05 M × 2 and 0.1 M × 2) by the

addition of salting buffer (2 M NaCl in 10 mM PB) every 20 min and heated 3 for 5 min in a water bath at 70 ℃ after each step to minimize the interactions between DNA bases and gold surface. After the salt-aging process, the solution was incubated overnight in an orbital shaker at room temperature. The solution was then centrifuged (12,000 rpm for 40-nm AuNPs, 10,000 rpm for 50-nm AuNPs and 8000 rpm for 60-nm AuNPs) for 10 min, respectively, and the supernatant was removed carefully to get rid of unmodified DNA and unreacted reagents. The precipitate was redispersed in 10 mM PB solution (pH 7.4; this procedure was repeated four times). For example, when 1 mL of DNA-modified solution was centrifuged under this condition,

2. Synthesis of Au-Au nanosnowmen

1% polyvinylpyrrolidone (PVP), 10mM Hydroxylamine(HA) and 5 mM Choloroauric acid in deionized water were used. DNA-modified 40-nm AuNPs were used as the seeds for the asymmetric growth of an AuNP on DNA-AuNPs. The molar ratio between the reductant and Au^{+} (HA/Au^{+}) was kept at 2. 100 μL of 75 pM DNA-modified 40-nm AuNP solution was reacted with 2.90 μL of 5 mM HAuCl4 solution in the presence of 50 μL of 1% PVP and 2.90

μL of 10mM HA, respectively. The resulting mixture was mildly pipetted for several seconds and put them into ice water(0 ℃). The reaction time was 2.5 hours. Finally, the solution was centrifuged at 4,500 rpm for 5 min to eliminate any unreacted residues. After removing the supernatant, synthesized nanoparticles were redispersed in deionized water for further measurement.

3. Mirco-Raman Setup

Micro-Raman setup. All the Raman analyses in solution state were performed with the Renishaw in Via microscope equipped with Leica microscope [20× objective lens (NA 0.40). HeNe laser (633 nm), and Renishaw WiRE 3.1 software] was used for data acquisition and control. The similar laser power (~4 mW) was used for the experiments. Typically, 10 μL of the Au-Au head-body nanosnowman solution was added in a glass fiber for the measurement.

4. Calculation of the Electromagnetic Fields for Au-Au head-body nanosnowmen

To analyze the electromagnetic field distributions and explore the interactions between electromagnetic waves and nanosnowman

structures, we used the 3D finite element method and solved the Maxwell equation (COMSOL multiphysics software with RF module). The relative 6 permittivities ($\varepsilon = \varepsilon' + i\varepsilon''$) by Johnson and Christy5 were used for gold −11.8 + 1.26i @ 633 nm and the relative permittivity of water by Hale and Querry6 was used (1.77 + 3.92 * 10−8 i @ 633 nm). From these values, the dielectric conductivities (σ) were obtained by using the following equation, $\varepsilon = \varepsilon' + i\sigma/\omega\varepsilon 0$. Here, $\varepsilon 0$ is the absolute permittivity and ω is the angular frequency ($\omega = 2\pi c/\lambda$). We fixed the relative permeability (μr) as 1 in this case. A nanosnowman was built in a 1000 nm x 1000 nm x 1000 nm water−medium cube. From the one face of the cube, linearly polarized plane waves with a wavelength of 633nm were incident on each particle. All the other faces of the cube were set as no scattering boundary condition. The mesh elements were > 700,000 for each case with a higher density of the mesh elements around the neck region.

3. Result and Discussion

3.1 Design and Synthesis of Au-Au Nanosnowmen

To synthesize a nanoprobe that emits a strongly amplified SERS signal that can be used for bioapplication, the structure must first be designed to generate a strong amplified electromagnetic field. The enhancement of the electromagnetic field is achieved by the plasmonic coupling between metals when the nanostructures are closely attached with a nanometer scale distance. Therefore, the nanosnowmen structure with nanocrevice, which allows amplification of field strength, has been synthesized by many people. However, the blunt nanocrevice structure has less than expected signal amplification efficiency. The nanosnowmen discussed in this paper can be said to have very sharp, even nanogap properties. Figure 3-1 (A) shows two steps to synthesize Au-Au nanosnowmen. The first step is the process of attaching DNA as a ligand to the citrate-capped AuNP. This process proceeds to attach the DNA tightly to the AuNP surface. Because the DNA backbone is phosphate, it has a negative charge, and thus the DNA strands are

electrostatically repulsive each other. The way to increase the DNA grafting density is gradual adding NaCl to 0.5M to counteract this repulsion. This allow the DNA to stick close together.

The second step is the process of growing the body part of nanosnowmen. This process is a process of reducing Au precursor to the surface of the head by the reducing agent hydroxylamine. However, nucleation can occur in several places on the surface of the head, and there are three reaction conditions that are important for limiting the nucleation site to one. The first is low temperature. This reaction proceeds under ice water bath. To prevent multi-nucleation, the reaction rate should be lowered. This is because the Au precursor overcomes the repulsion of DNA and can receive multi-nucleation if it receives energy above the activation energy to nucleate. The second is low pH. The hydroxylamine, a reducing agent used in this reaction, is affected its reducing power depending by changing pH. The higher the pH, the faster the reaction rate and slower at lower pH. In Au-Au Snowmen synthesis, the reaction proceeds at pH 3.0 because of the lower rate required. Under pH 3.0, aggregation of nanoparticles can occur. The type of buffer is also important. Buffer that can be strongly coordinated to the surface of AuNP may affect the structure of the reaction product and is therefore not used. For example, the citrate buffer was not

suitable for this reaction by generating a by-product in the form of a nanoprism in the body part. Using various buffers, glycine buffer gave the best results. The final condition is DNA grafting density. The DNA grafting density is discussed in more detail in the next chapter, the mechanism study. Figure 2-1 (B) shows the TEM image of the product when 5'-A (Adenine) $_{20}$-Cy3-SH-3' was used and when using 5'-T (Thymine) $_{20}$-Cy3-SH-3'. When A_{20} and T_{20} were used, the nanosnowmen were synthesized with high yield. When the TEM image was enlarged, the nanocrevice part was sharply cut in the case of A_{20}, and even Nanogap was observed. However, when T_{20} is used, it shows that nanocrevice is a blunt form, and quite wide parts are fused together between head and body. The reason why the nanostructures are different for these two cases will be discussed in the next topic, the mechanistic study.

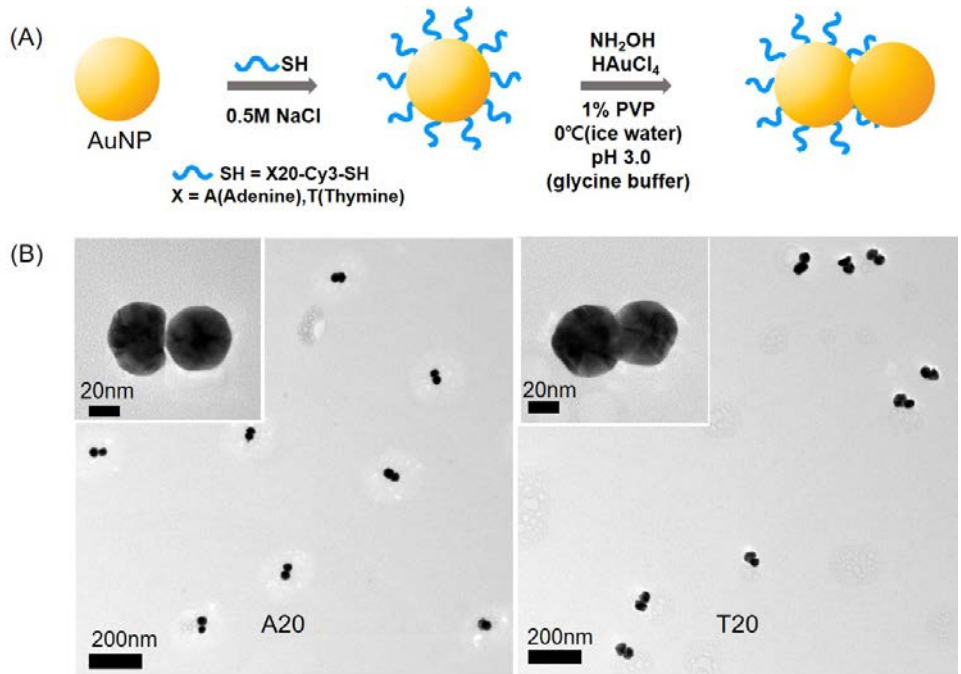

Figure 3-1. (A) Reaction scheme of Au-Au nanosnowmen synthesis (B) TEM image of nanosnowmen : Reaction product using A(Adenine)$_{20}$-Cy3-SH DNA(left), Using T(Thymine)$_{20}$-Cy3-SH DNA(right)

3.2 Mechanistic Study of Nanosnowmen Growth

We will go into more detail about the mechanism of synthesis of nanosnowmen. The most important part of the reaction conditions discussed in 3.1 is DNA grafting density. The DNA backbone is negatively charged because it is composed of phosphate. $HAuCl_4$, the precursor of Au, is also negatively charged because it is present in aqueous solution in the form of $AuCl_4^-$. Therefore, inevitably, the DNA and Au precursors adhered to the AuNP must be repelled by the repulsive force, which interferes with the nucleation process on the AuNP surface. Because of this interruption, when the nucleation occurs, the Au precursors are continuously reduced to the body part of the Nanosnowmen, where the nuclei are exposed to the outside, where no DNA is attached. Figure 3-2 (A) shows the TEM image of how the main product changes with increasing DNA grafting density. As DNA grafting density increases, the number of nucleation sites decreases, which can be confirmed by Figure 3-2 (B). The reason why the number of nucleation sites is decreasing is explained in the figure which is briefly described in Figure 3-2 (C). Figure 3-3 depicts how the structure of the Nanocrevice is different when using the A_{20} sequence and when using the T_{20} sequence. Before starting this discussion, you should be aware that

the four bases of DNA interact differently with the surface of the AuNP. The basic interaction strength is known as A> C> G> T.

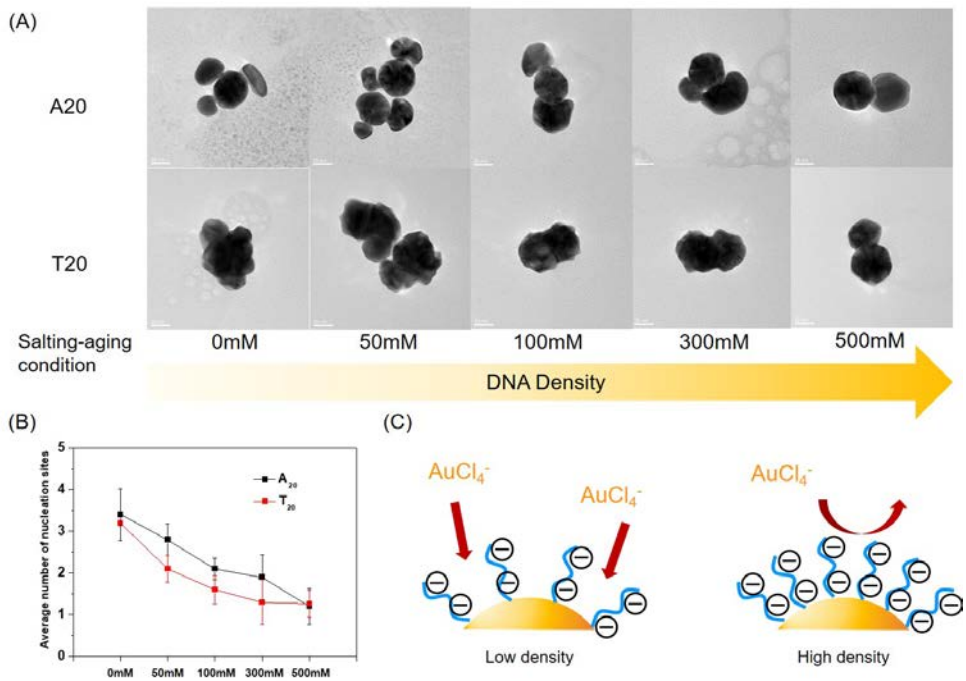

Figure 3-2. (A) Changes in Nanosnowmen Main Product Structure with Increasing DNA Grafting Density (B) The number of bodies created in the snowmen head part as DNA grafting Density Increases (C) Scheme Describing the Different Accessibility of Precursors as DNA Grafting Density Increases

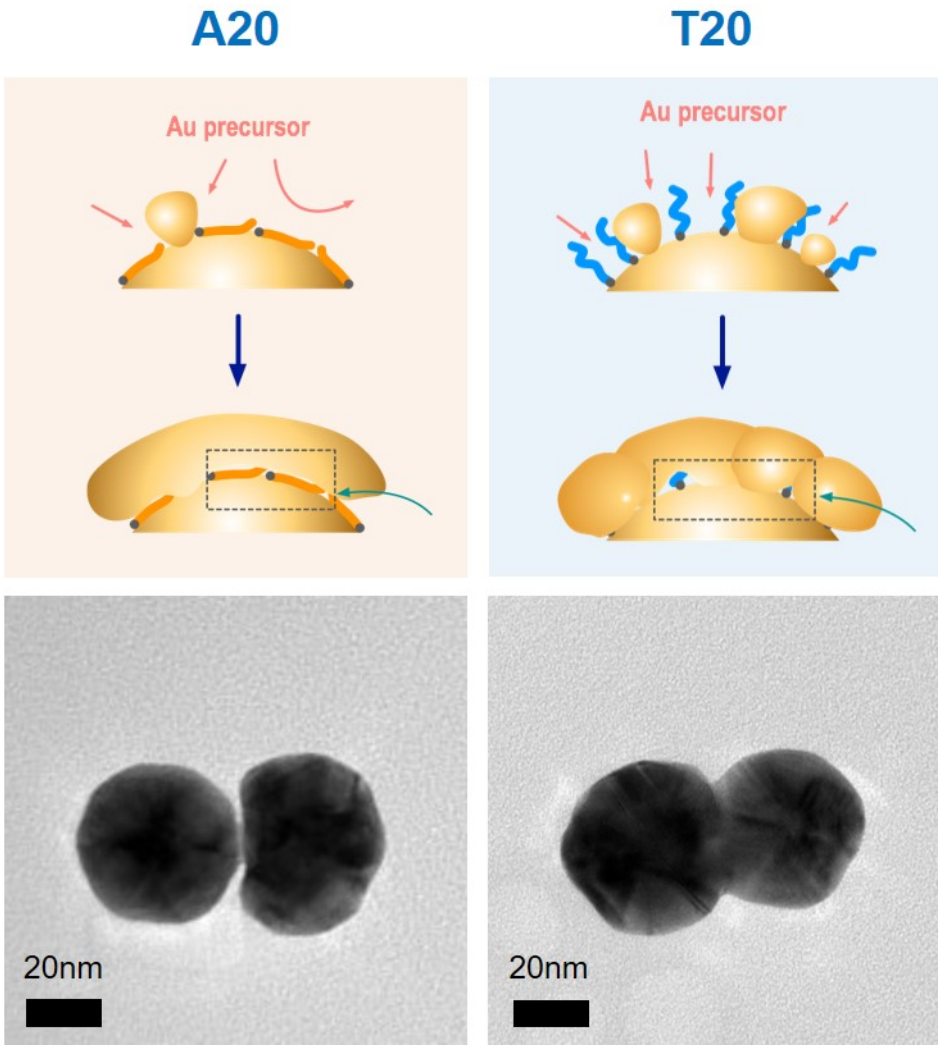

Figure 3-3. Changes of Nanocrevice structure by DNA base changes : Adenine(left), Thymine(right)

Especially, in the case of A, there is a lot of Nitrogen, and the electron cloud scattered on the nitrogen strongly interacts with the Au surface, so that the A_{20} chain lies on the surface and sticks to the surface. Therefore, when A_{20}-Cy3-SH is attached to an AuNP ligand, there is not much exposed space where nucleation can occur on the surface. When the body grows, a gap is formed due to the A_{20} chain and the body grows. The part of this Nanogap plays the main role of making the sharpened Nanocrevice. On the other hand, when the T_{20}-Cy3-SH is attached, the T_{20} chain does not wrap the Au surface because the thymine does not interact with the Au surface. Therefore, the Au precursor will form a nanocrevice structure in a blunt form. The difference in the structure of these nanocrevice leads to differences in optical properties.

3.3 Optical Properties of Au-Au Nanosnowmen with ~1nm Nanogap

In the previous chapters, we looked at how the structure of nanocrevice changed depending on the type of DNA base used in the synthesis. In this chapter, I will explain how these small structural differences make a difference in optical properties. Figure 3-4 (A) shows the intensity of the amplified electromagnetic field in the nanocrevice through simulation. The left side is the nanosnowmen with Adenine and the right side is synthesized with Thymine. It was predicted that the use of A_{20} with sharp nanocrevices would strongly amplify the intensity of the electromagnetic field. In general, the intensity of SERS is proportional to the fourth power of the electromagnetic field strength. When A_{20} is used, the intensity of the electromagnetic field in the nanocrevice portion is about twice as high as that in the case of using T_{20}. Figure 3-4 (C) shows the SERS spectrum measured experimentally. The intensity will be compared based on 1198cm^{-1}. A_{20} showed 11 ~ 12 times higher SERS signal intensity than T_{20}. This shows some degree of correspondence with the simulation results. Figure 3-4 (D) is a histogram

showing the quantitative comparison of signal intensity differences shown in Figure 3-4 (B).

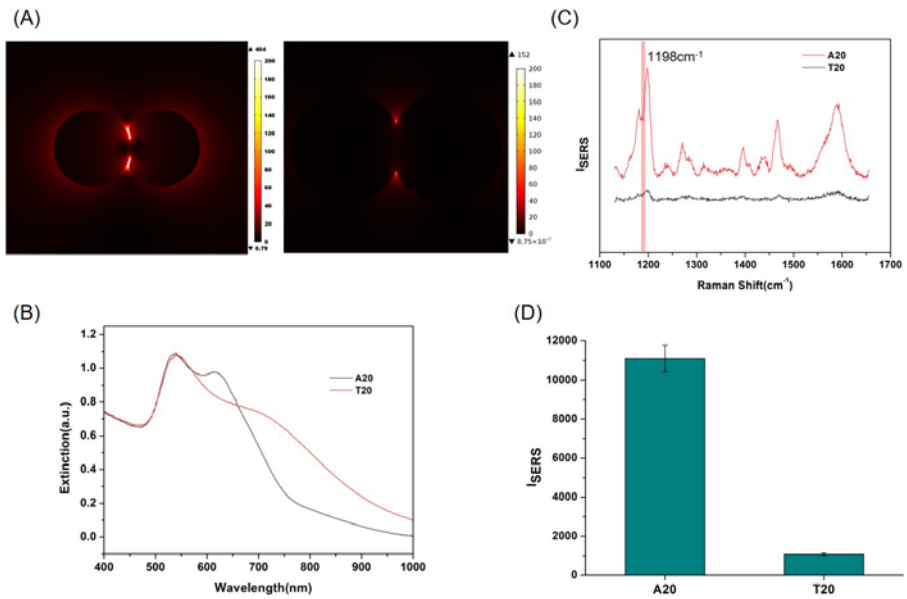

Figure 3-4. (A) Comparison of Electromagnetic Field Strength of nanocrevice Region Using Adenine DNA and Thymine DNA (B) UV-vis extinction Spectrum (C) SERS spectra of Cy3 dyes on nanosnowmen from A_{20} and T_{20} DNA sequences at 633 nm excitation wavelength. (D) SERS intensity comparison between nanosnowmen using A_{20} sequence and T_{20}. SERS spectra in these figures were taken with ~4 mW laser power, 30 s acquisition time, 20× objective lens, and 100 pM particle concentration.

It is very encouraging that the structure of the nanocrevice changes as the DNA attached to the head changes, and the intensity of the SERS signal differs by more than 10 times. To calculate the correct enhancement factor, 40 nm AuNP with A_{20} and 40 nm diameter AuNP with T_{20} were treated with DTT (Dithiothreitol), and all the DNA was extracted and quantified by Cy3 fluorescence signal , modified to the DNA. As a result, 353 of A_{20}-Cy3-SH DNA were coordinated to AuNP surface and 427 of T_{20}-Cy3-SH DNA were coordinated. The calculated enhancement factor is 4.3×10^{9} for A_{20} and 1.7×10^{8} for T_{20}.

3.4 SERS Signal Stability of Au-Au Nanosnowmen in Biofluid

If a typical Raman dye is exposed to the outside, there is a vulnerability that the dye may be damaged or broken by the external environment and the SERS signal may be reduced. But Au-Au nanosnowmen can protect the Raman dye with nanocrevice like nanogap. To confirm this, ligand exchange reactions were carried out with various nanoprobes including nanosnowmen. The nanoprobes used in this experiment are A_{20} nanosnowmen, T_{20} nanosnowmen, Au-Nanobridged-Nanogap Particles, and thiolated DNA capped AuNP. In A_{20} nanosnowmen, the trapped dye remained in the nanocrevice region, resulting in a signal reduction of only 13%. Because the outer DNA was detached by PEG.

For the T_{20} Raman dye, the signal was reduced by 68%, because the nanocrevice was so thick that it could not trap large amounts of dye. Since AuNNP has a nanogap in it, there is no signal loss. Thiolated DNA-capped AuNP is predicted to break off most of the dye, which can be seen in Figure 3-5. To be used in bioapplication, signal stability should be ensured in an environment like invivo. Figure 3-6 (A) shows how the SERS signal changes after

dispersing nanosnowmen in human serum and incubating for 16 hours. In 1% Human Serum, neither of the SERS signals decreased significantly in both cases. In the case of 50% Human Serum, only the A_{20} nanosnowmen signal was retained and the T_{20} nanosnowmen lost the signal.

Signal stability was tested in the presence of human serum as well as glutathione. glutathione is a substance with strong reducing power and exists at a high concentration in the liver in vivo. Therefore, it is meaningful to test whether the signal is stable in 1 mM glutathione. SERS signal was measured after incubation in 1 mM glutathione solution for 16 hours. As a result, the A_{20} nanosnowmen signal decreased by only 9.7%, while the T_{20} nanosnowmen signal disappeared. Through this, we can conclude that nanocrevice with Nanogap properties is helpful in the stability of the SERS signal and that A_{20} nanosnowmen can be used for bioapplication.

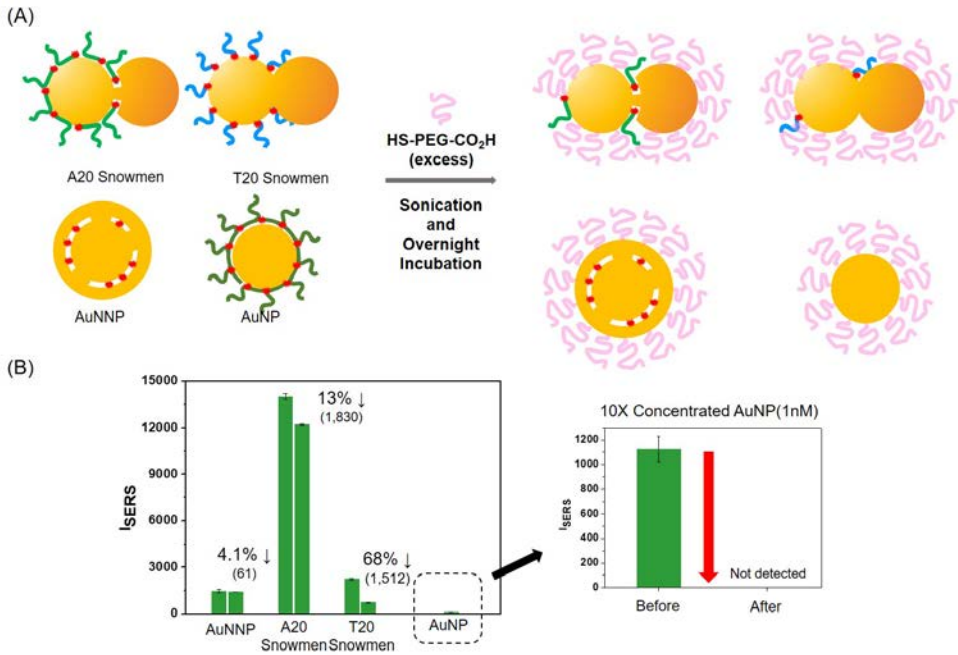

Figure 3-5. Resistance of raman dyes inside nanogap to desorption (A) Scheme showing DNA desorption of surface by ligand substitution reaction of various nanoprobe (B) Comparison of SERS signal intensity before and after DNA desorption. Spectra in these figures were taken with ~4 mW laser power, 30 s acquisition time, 20× objective lens, and 100 pM particle concentration.

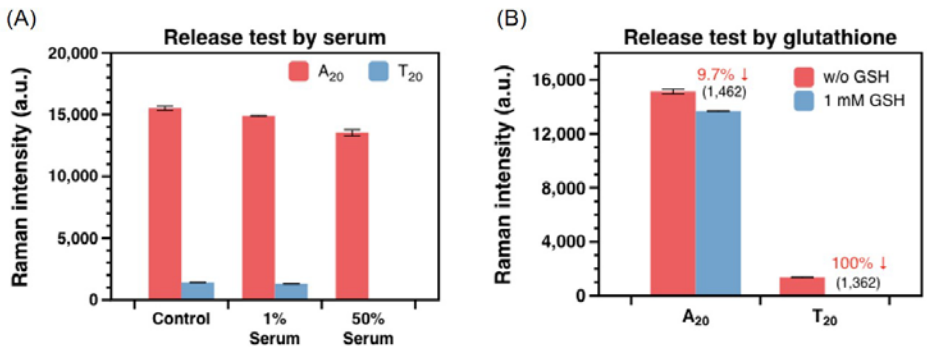

Figure 3-6. (A) Comparison of SERS signal intensity before and after 16hours in 1%, 50% Human Serum (B) Comparison of SERS signal intensity before and after 16hours in 1mM glutathione solution

4. Conclusion

Au-Au nanosnowmen with nanocrevice of nanogap shape was synthesized by growing a Au body with a AuNP having a diameter of 40 nm with a DNA having a sequence of A_{20}-Cy3-SH as a head. The nanosnowmen synthesized using A_{20}-Cy3-SH DNA have 11 times stronger SERS signal intensity than the nanosnowmen synthesized using T_{20}-Cy3-SH. Simulation of the electromagnetic field distribution using the Comsol program showed that the nanocrevice with nanogap shape had a strong electromagnetic field strength of about 2.3 times. The nanosnowmen synthesized using A_{20}-Cy3-SH was calculated to have an enhancement factor of 4.3 X 10^9 and a nanosnowman of T_{20}-Cy3-SH of 1.7 X 10^8. In order to test the signal stability in Biofluid, the change of SERS signal intensity of nanosnowmen in 1%, 50% human serum, 1 mM glutathione solution was measured. As a result, nanosnowmen used A_{20}-Cy3-SH was protected with Raman dye by nanogap, The loss was insignificant.

Reference

1. El-Sayed MA. Acc Chem Res 2001, 34:257-264.

2. Jensen TR, Malinsky MD, Haynes CL, Van Duyne RP. J Phys Chem B 2000,104:10549-10556.

3. Kelly KL, Coronado E, Zhao LL, Schatz GC. J Phys Chem B 2003, 107:668-677.

4. Xia Y, Halas NJ. MRS Bull 2005, 30:338-344.

5. Daniel MC, Astruc D. Chem Rev 2004, 104:293-346.

6. Rosi NL, Mirkin CA. Chem Rev 2005, 105:1547-1562.

7. Jackson JB, Halas NJ. J Phys Chem B 2001, 105:2743-2746.

8. Alivisatos AP, Johnsson KP, Peng XG, Wilson TE, Loweth CJ, Bruchez MP, Schultz PG. Nature 1996, 382: 609-611.

9. Claridge SA, Goh SL, Frachet JMJ, Williams SC, Micheel CM,

Alivisatos AP., Chem Mater 2005, 17:1628-1635.

10. Storhoff JJ, Lazarides AA, Mucic RC, Mirkin CA, Letsinger RL, Schatz GC. J Am Chem Soc 2000, 122:4640-4650.

11. Nam J-M, Stoeva SI, Mirkin CA. J Am Chem Soc 2004, 126:5932-5933.

12. Yao X, Li X, Toledo F, Zurita-Lopez C, Gutova M, Momand J, Zhou F., Anal Biochem 2006, 354:220-228.

13. Li H, Rothberg L. Proc Natl Acad Sci U S A 2004, 101:14036-14039.

14. Willets KA, Van Duyne RP. Ann Rev Phys Chem 2007, 58:267-297.

15. Lee J-H, Nam J-M, Jeon K-S, Lim D-K, Kim H, Kwon S, Lee H, Suh YD. ACS Nano 2012, 6:9574-9584.

16. Savage KJ, Hawkeye MM, Esteban R, Borisov AG, Aizpurua J, Baumberg JJ., Nature 2012, 491:574-577.

17. Esteban R, Borisov AG, Nordlander P, Aizpurua J. Nat. Commun. 2012, 3:825.

18. Kneipp K, Kneipp H, Itzkan I, Dasari RR, Feld MS. Chem Rev 1999, 99:2957-2976.

19. Kneipp J, Kneipp H, Kneipp K. Chem Soc Rev 2008, 37:1052-1060.

20. Nie S, Emory SR. Science 1997, 275:1102-1106.

21. Ming T, Zhao L, Yang Z, Chen H, Sun L, Wang J, Yan C. Nano Lett 2009, 9:3896-3903.

22. Graham D, Thompson DG, Smith WE, Faulds K. Nat Nanotech 2008, 3:548-551.

23. Lim D-K, Jeon K-S, Kim HM, Nam J-M, Suh YD. Nat Mater 2010, 9:60-67.

24. Lim D-K, Jeon K-S, Hwang J-H, Kim HK, Kwon SH, Suh YD, Nam J-M., Nat Nanotech 2011, 6:452-460.

25. Nam J-M*, Oh J-W, Lee HM, and Suh Y-D*, Accounts of Chemical Research, 2006, 49, 2746.

Au-Au Nanosnowman with ~1nm Nanocrevice Gap Control by DNA Sequence

DNA 염기서열 변화에 따른 금-금 눈사람 나노구조체의 나노크레비스 갭 특성 조절

국문 초록

다양한 타겟 물질들, 특히 바이오 물질들을 검출하는데 있어서 강한 광학적 신호를 내는 나노프로브를 이용하는 것은 현재 뿐만 아니라 미래에도 각광받을 기술 중 하나이다. 이 검출 방법에 있어서 가장 중요한 것은 일관된, 강한 신호를 내는 나노프로브를 합성하는 것이다. 금속 나노입자의 대표적인 성질인 국소 표면 플라즈몬 공명(Localized Surface Plasmon Resonance, LSPR)은 금속 나노입자가 강하게 증폭된 표면증강라만산란(Surface Enhanced Raman Scattering, SERS) 혹은 형광 신호를 내게 하는데 있어 매우 중요한 역할을 한다. 주된 광학 신호의 증폭은 나노미터의 거리를 사이에 둔 접합부분이나 나노미터 수준의 금속 나노입자 사이의 틈새에서 발생하는 플라즈몬 짝지음 현상에 의해 발생한다. 플라즈몬 짝지음 이 일어나면, 나노미터 수준의 틈새에 전자기장의 세기가 강하게 증폭되며, 증폭된 전자기장의 영역안에 광학 신호물질이 위치했을 경우, 매우 강하게 증폭된 광학신호를 얻을 수 있다. 이 논문에서는 금-금 나노스노우맨 구조체를 고수율로 합성하는 방법에 대해 다룬다. 합성 과정 중 나노 스노우맨의 머리 부분에 부착되는 DNA

의 염기종류를 변화시켜 노스노우맨의 머리-몸 접합부분의 미세구조를 조절할 것이며, 이에 따라 변하는 나노스노우맨 구조체의 광학적인 성질에 대해서 논하였다. 또한 추후 바이오 분야에서의 응용을 위해서 생체 내 환경에서 나노스노우맨이 발생시키는 신호의 안정성 또한 검증하였다.

핵심어 : 플라즈모닉스, 나노프로브, 플라즈몬 짝지음, 국소 표면 플라즈몬 공명, 표면 증강 산란, DNA 서열,

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