

The Study of Surface Plasmonic Bands Using Block Copolymer Nanopatterns

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블록공중합체 나노패턴을 이용한 표면 플라즈몬 연구

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Abstract It is important to develop a simple method of tuning localized surface plasmon resonance(LSPR) properties, due to their numerous applications. In addition, the careful examination of the shape, size and combination of metal nanoparticles is useful for understanding the relation between the LSPR properties and metal nanostructures. This article describes the dependence of the LSPR properties on the arrays of metal nanoparticles obtained from a block copolymer(BCP) micellar thin film. Firstly, two different Au nanostructures, having a dot and ring shape, were fabricated using conventional block copolymer micelle lithography. Then, Ag was plated on the Au nanostructures through the silver mirror reaction technique to obtain Au/Ag bimetallic nanostructures. During the production of these metallic nanostructures, the processing factors, such as the pre-treatment by ethanol, silver mirror reaction time and removal or not of the BCP, were varied. Once the Au nanoparticles were synthesized, Ag was properly plated on the Au, providing two distinguishable characteristic plasmonic bands at around 525nm for Au and around 420nm for Ag, as confirmed by the UV-vis measurements. However, when a small amount of Au seed nanoparticles, which accelerate the Ag plating speed, was formed by using a block copolymer with a relatively high molecular weight, all of the Au surfaces were fully covered by Ag during the silver mirror reaction, showing only the characteristic peak for Ag at around 420nm. The Ag plating technique on Au nanoparticles pre-synthesized from a block copolymer is useful to study the LSPR properties carefully.

요약 다양한 응용분야를 가진 국부적인 표면플라즈몬 공명 특성을 손쉽게 제어할 수 있는 기술 개발은 매우 중요하다. 또한, 금속 나노입자의 형태, 크기, 그리고 조합에 관한 세심한 조사는 공명특성과 금속 나노구조의 관계를 이해하는데 매우 유용하다. 본 논문은 블록공중합체 마이셀 박막을 이용하여 얻어진 금속나노입자 배열에 따른 국부적인 표면플라즈몬의 공명특성에 관한 연구이다. 우선 전통적인 방법의 블록공중합체 리소그래피를 통해 두 가지 다른, 점 형태 및 링 형태, 금 나노입자를 제조하였다. 그 다음 은거울 반응을 통하여 금 나노입자위에 은이 둘러 쌓이도록 금/은 이중금속 나노구조를 구현했다. 금속 나노 구조체 조절을 위해 에탄올 전처리, 은거울 반응 시간, 블록공중합체의 제거 유무 등의 공정변수를 변화시켰다. 초기 금 나노입자가 잘 제조된 경우 항상 금나노입자 표면에 적절히 은이 잘 형성되었고, 이는 UV-Vis 실험에서 각 금속나노 입자의 고유 플라즈몬 밴드인 금 525nm, 은 420nm 에서 각각 나타났다. 하지만 최초 적은 양의 금 나노입자가 제조되었을 경우 은 도금 속도가 빨라져서, 초기 금 나노입자의 표면을 은이 완전히 덮었으며, 이는 UV-Vis 실험에서 금의 플라즈몬 밴드는 나타나지 않고, 은의 고유 플라즈몬 밴드만 420nm에서 나타났다. 블록공중합체로부터 미리 합성된 금나노 입자 위에 은을 도금하는 방법은 국부적인 표면플라즈몬 특성을 면밀히 조사하는데 매우 유용하다.

Keywords : Au/Ag bimetallic nanoparticles, block copolymer micelle lithography, block copolymer nanopattern, localized surface plasmon band, silver mirror reaction.

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1. Introduction

Owing to localized surface plasmon resonance (LSPR) properties of the metallic nanoparticles, it has attracted considerable attention in various applications including chemical sensor, drug delivery, photo-thermal cancer therapy, polymer solar cell, surface-enhanced Raman scattering, fluorescence resonance energy transfer[1]. In general, such LSPR bands are strongly affected by particle size, shapes, dielectric medium and particle-particle distance[2]. Numerous synthetic approaches have been proposed to obtain homogeneous metallic nanoparticles in size and shape, which would guarantee reproducible LSPR characteristics[3, 4].

Tuning of LSPR bands using BCP micelles can be done easily by varying metal precursors into the core region. More complex plasmonic bands such as dual band or triple band also can be achieved by mixing different BCP micelle solution containing different metal precursors[5]. Another method is to use metal alloy by adopting more than two different metal precursors. Depending on the ratio of metal precursors, LSPR bands can be tuned[6]. Recently, we reported ring-shaped Au/Ag metallic nanoparticles that prepared by Ag deposition on Au nanoparticle[7]. With increasing Ag amount, LSPR band was gradually shifted to the Ag characteristic band from Au band. This solution-based metal deposition technique could be one of good candidate for controlling LSPR band.

In this paper, we demonstrate how LSPR bands are varied depending on initial BCP micellar structures based on metal deposition technique. We used PS-*b*-P2VP amphiphilic block copolymer consisting of P2VP core and PS corona. Then, we controlled BCP nanopattern by treating either selective solvent or not. BCP mother pattern makes same Au nanopattern, and Ag deposition was carried out during various time. At the end of paper, we introduce specific case showing broad LSPR band in all visible region, which may be useful for some optical device applications.

2. Experimentals

2.1 Materials

Polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) diblock copolymer ($M_n^{PS}=440\text{kg/mol}$, $M_n^{P2VP}=353\text{kg/mol}$, $M_w/M_n=1.19$) and PS-*b*-P2VP ($M_n^{PS}=133\text{kg/mol}$, $M_n^{P2VP}=132\text{kg/mol}$, $M_w/M_n=1.15$) were purchased from Polymer Source and used without further purification. A PS-*b*-P2VP copolymer was dissolved in *o*-xylene (Sigma-Aldrich) at room temperature to make a 0.4 wt% polymer solution. To obtain the block copolymer micellar thin films, the PS-*b*-P2VP solutions were spin-coated at 3000 rpm for 1 min onto glass substrates.

2.2 Fabrication of metal nanostructures

PS-*b*-P2VP micellar thin films were treated in ethanol bath for 3 min to obtain ring-shaped structures. Note that ethanol treatment was not performed for dot-shaped structures. The thin films were dipped into an Au precursor solution (0.1 wt% HAuCl₄ in ethanol) for 3min to bind the Au salts inside the P2VP blocks. Excess Au salts were removed by rinsing with deionized water several times. After drying, the films were exposed to a hydrogen plasma environment (Femto Plasma Cleaner, 100watts) for given time to reduce Au ions to Au metals and to remove polymers. From the films containing Au nanoparticles, Au/Ag bimetallic nanostructures were prepared via Ag mirror reaction using the Tollens reagent that was obtained by adding 0.3 mL of 0.1 M aqueous solution of NaOH to 4 mL of 0.25 M aqueous solution of AgNO₃. The quickly formed silveroxide was dissolved by titrating with 40wt% aqueous ammonia until the black silveroxide particles disappeared and the [Ag(NH₃)₂]⁺ complex were formed. For Ag mirror reaction, the films containing Au nanoparticles were immersed in a mixture of 50 mL of Tollens reagent and 50 mL of 10 wt% glucose in 15 mL H₂O for various times to grow Ag nanoparticles onto the Au nanoparticles. The Ag growth was stopped by removing the glass substrates

with Au/Ag nanostructured films from the solution, and the substrate was quickly immersed into pure H₂O

2.3 Characterization of Au/Ag nanostructured films

The PS-*b*-P2VP micellar templates and nanostructured Au/Ag bimetallic nanostructures were characterized by a scanning electron microscope (SEM, NanoSEM 230, FEI) operating at 5 kV without any metal coating. UV-Vis-IR measurements for surface plasmon resonance absorbance were performed with a Varian Carey 5000 (Agilent) spectrophotometer. All measurements of Au/Ag nanostructured films were carried out in air.

3. Results and Discussion

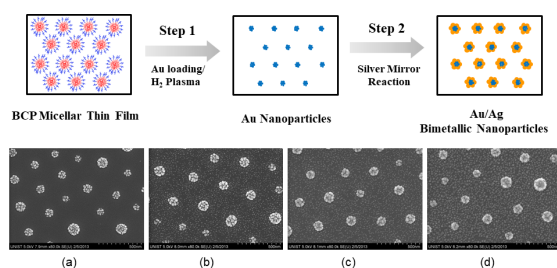


Fig. 1. Top: Schematic illustration. Bottom: SEM images of (a) dot-shaped Au seed nanoparticles and Au/Ag bimetallic nanoparticles obtained from silver mirror reaction for (b) 40 sec, (c) 80 sec and (d) 120 sec.

Figure 1 describes a fabrication process of Au/Ag bimetallic dot arrays by using block copolymer micellar thin films. As-spun micellar thin film is spherical type consisting of P2VP cores and PS coronas. The thin films are immersed in ethanol bath containing Au precursor which can bind with pyridine moiety of the micelle cores. After hydrogen plasma treatment for 3min, block copolymer is removed and Au ions are reduced into pure Au nanoparticles. Figure 1(a) shows dot-shaped Au nanoparticles which are located in P2VP core region of the original micellar thin films. And we clearly see that many small Au

nanoparticles are formed rather than big nanoparticle in one P2VP core. This is general phenomena in a block copolymer micellar system, because P2VP polymer chains exist among the Au precursors, limiting the formation of big nanoparticles. To obtain Au/Ag bimetallic nanostructures, the thin film containing Au nanoparticles was immersed in a mixture of Tollens reagent and glucose solution for 40, 80 and 120sec. As immersing time increases, more Ag are deposited. Figure 1(b)-(d) shows that the original surface of the nanoparticles is getting smooth as immersing time goes. It indicates that Ag is well plated on the surface of the Au nanoparticles.

To confirm evidence of Ag plating on Au nanoparticles, we measured UV-vis spectra for all samples and displayed in Figure 2. Au seed particles do not give a clear Au plasmonic peak around 525nm due to relatively small amount of Au compare to Au/Ag bimetallic nanostructures.

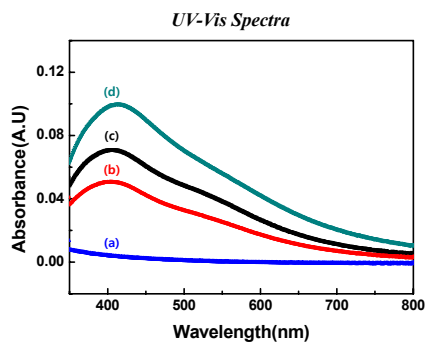


Fig. 2. UV-Vis spectra of dot-shaped nanoparticles. (a) Dot-shaped Au seed nanoparticles. Ag plating was carried out for (b) 40 sec, (c) 80 sec and (d) 120 sec.

However, as plating time increases, Au peak intensity becomes stronger, and new peak around 420nm for Ag surface plasmonic band appeared. This is direct evidence of Ag plating on Au nanoparticles. And it indicates that Au/Ag nanostructures are not alloy which generally makes single plasmonic peak depending on its composition ratio[6]. Therefore, it indicates that this Ag plating system properly provides

Au/Ag bimetallic nanostructures consisting of Au nanoparticles covered by Ag metal.

Next, ring-shaped Au/Ag bimetallic nanoparticles were fabricated and the procedures are shown in Figure 3. Initial structure of the micellar thin film consisting of P2VP cores and PS coronas is changed into dimple-like structure by ethanol treatment. The P2VP cores are swelled by ethanol which is good solvent for P2VP and non-solvent for PS, then quick drying ethanol makes the P2VP chain shrunk, leaving holes in the middle of the P2VP cores[8]. Next, the dimple-like-structured thin film was immersed in Au precursor-containing solution for 3min and subsequent hydrogen plasma treatment reduces Au precursors to Au metal.

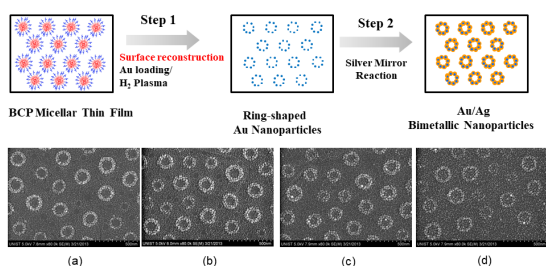


Fig. 3. Top: Schematic illustration. Bottom: SEM images of (a) ring-shaped Au seed nanoparticles and Au/Ag bimetallic nanoparticles obtained from silver mirror reaction for (b) 30 sec, (c) 60 sec and (d) 90 sec.

Figure 3(a) shows uniform ring-shaped Au nanoparticles. The rings with thick wall were fabricated because relatively high molecular weight polymer (793k/mol) was used. High molecular weight P2VP chain can accommodate enough Au precursors, which leads to many Au nanoparticles with thick wall. Consequent silver mirror reaction makes Au/Ag bimetallic nanoparticles as shown in Figure 3(b)-(d). As Ag plating time goes from 30 to 90sec, Ag was plated on the Au nanoparticles, indicating that individual nanoparticle became bigger.

Figure 4 displays UV-vis spectra of ring-shaped Au/Ag bimetallic nanoparticles. The weak and broad

peak around 525nm is seen for original ring-shaped Au nanoparticles. It indicates that many different sizes of Au nanoparticles were formed and the amount of Au nanoparticles was not enough.

At a short Ag plating time of 30sec and 60sec, Au peak intensity got stronger, but still Ag peak around 420nm did not appear. This result may be explained that the speed of Ag plating is slow compared to dot-shaped Au nanoparticles. At Ag plating time of 90sec, Ag plasmonic peak around 420nm appeared with high intensity and also Au plasmonic peak still remained. Compared to dot-based Au/Ag bimetallic nanoparticles as seen in Figure 2, the ring-shaped Au/Ag bimetallic nanoparticles provided broader plasmonic band ranging from 400 to 500nm. We expect that small amount of Au nanoparticles affecting Au LSPR property around 525nm are not completely covered by Ag due to unfavorable structures to be plated compared to dot-shaped nanostructures.

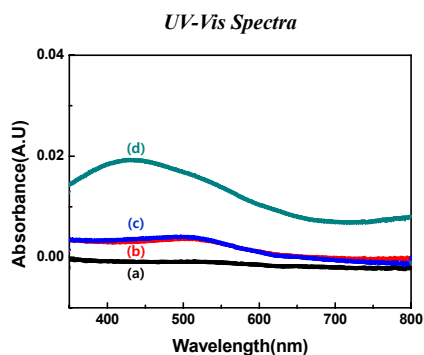


Fig. 4. UV-Vis spectra of ring-shaped nanoparticles. (a) ring-shaped Au seed nanoparticles. Ag plating was carried out for (b) 30 sec, (c) 60 sec and (d) 90 sec.

Lastly, we tried to make a very broad plasmonic band which is useful for some optical devices or analysis tools such as polymer solar cell, Surface Enhanced Raman Spectroscopy (SERS). In order to arrange high density of the nanoparticles, a relatively small molecular weight of PS-*b*-P2VP block copolymer was used and ethanol treatment that induces ring-shaped

structure was not performed. In addition, a plasma treatment time was 12sec. This induces many small Au nanoparticles, and also block copolymer is not removed completely. In general, long plasma treatment time, for example 3min, leads aggregation of small nanoparticles, resulting small amount of big Au nanoparticles. That's the why plasma treatment time of 12sec makes high amount of small Au nanoparticles. Then, Ag mirror reaction time was controlled to plate Ag on the Au nanoparticles.

Figure 5(a) shows that many small block copolymer micelles with the size of ~100nm were formed compared to Figure 1(a) utilizing high molecular weight block copolymer. Also, many Au nanoparticles were positioned on the surface of the block copolymer micelles. This result was confirmed by UV-vis spectra in Figure 6(a). A small shoulder peak around 525nm, Au plasmonic band, is clearly seen, which is not detected in Figure 1(a) due to few population of Au nanoparticles. It indicates that more Au nanoparticles were introduced when smaller block copolymer was used.

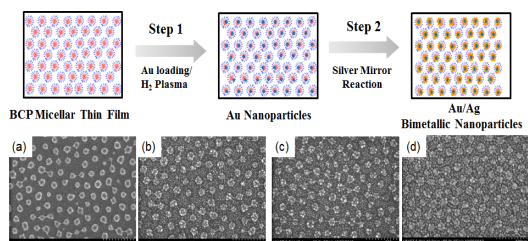


Fig. 5. SEM images of (a) Au seed nanoparticles obtained from small molecular weight of block copolymer. Ag plating was carried out for (b) 30 sec, (c) 60 sec and (d) 90 sec.

When block copolymer thin film containing Au nanoparticles was immersed in Ag plating solution, Ag was gradually plated on the Au surfaces depending on immersing time. Figure 6(b)-(d) shows that the density of the Au/Ag bimetallic nanoparticles was increased as Ag treatment time increased. To verify plasmonic properties for Au/Ag bimetallic nanoparticles UV-vis measurement was conducted. After Ag plating for

30sec, a highly broad plasmonic band covering all visible regions was obtained, providing a new Ag plasmonic band around 420nm. Because many initial Au nanoparticles induce proper amount of Ag plating on the surface of Au nanoparticles during Ag mirror reaction. In addition, there is some possibility of remaining Au nanoparticles inside of BCP micelles, which can contribute strong Au characteristic peak. Compare to the former experiment, Figure 2 and 4, the pattern of plasmonic band in Figure 6 is completely different. In figure 2 and 4, as Ag plating time increased, Ag plasmonic peak was remarkable, but Au plasmonic peak around 525nm also got strong in figure 6 due to high amount of initial Au population and remaining Au nanoparticles inside BCP micelles.

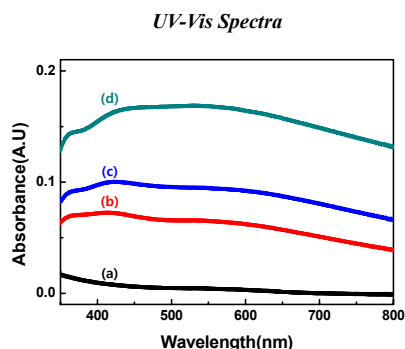


Fig. 6. UV-Vis spectra obtained from small molecular weight of block copolymer. (a) Au seed nanoparticles. Ag plating was carried out for (b) 30 sec, (c) 60 sec and (d) 90 sec.

This is possible only when Au and Ag are combined as a form of bimetallic structure, not alloy. When Ag plating time increased, similar plasmonic pattern was developed. But, owing to high density of Au/Ag bimetallic nanoparticles, it showed too high absorbance value.

4. Conclusion

In conclusion, we investigated localized surface plasmonic band for various Au/Ag bimetallic

nanostructures fabricated by block copolymer micelles. Some factors affecting final nanostructures such as initial micellar structures, Ag plating time, molecular weight of block copolymer were controlled. In most of cases, when Ag was plated on Au seed particles through silver mirror reaction, the intensity of Ag plasmonic band was dominant, suggesting that Ag covered the surfaces of the Au seed nanoparticles. However, when the population of the Au seed nanoparticles was increased by adopting relatively small molecular weight of block copolymer, a moderate amount of Ag was plated on each Au seed nanoparticles, providing broad plasmonic band covering all visible regions. Conventional block copolymer micelle technique in combination with silver mirror reaction allows diverse Au/Ag bimetallic nanostructures which can control surface plasmon resonance band.

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<Research Interests>

Synthesis of metal nanoparticles based on block copolymer, Separator membranes for energy applications, Anode materials for Li-ion batteries