Fabrication of Au Nanoparticles Array with Nanogaps based on a Sea-island Structure of a Block Copolymer film

Daiki Yamanishi¹, Shota Naka¹, Tatsuya Shoji¹, Taka-Aki Asoh², Yasuyuki Tsuboi^{1*}

¹Graduate school of Science, Osaka City University, Sugimoto, 3-3-138, Sumiyoshi, Osaka, 558-8585, Japan

²Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan,

E-mail: twoboys@sci.osaka-cu.ac.jp

In accordance with a great progress of nanotechnology, fundamentals and applications of surface plasmon and related science and technology underwent an explosive development. Nowadays, it is called "*plasmonics*". In plasmonics, metallic nanoparticles or metallic films with nanostructures have been used to efficiently excite localized surface plasmon (LSP). In particular, a nanoparticles dimer or a nanostructure with a nanometer-sized "gap" has a special function to strongly localize an electromagnetic field of incident light around the gap. It is called "gap-mode" LSP and has been an important basis of plasmonic applications such as SERS, energy conversion [1], and optical trapping [2]. For further development of plasmonics, it is indispensable to establish a methodology to supply a large amount of solid substrate with a function of gap mode LSP.

So far, in a laboratory level, the technique of electron beam lithography has frequently been used for fabricating such plasmonic bow-tie and nano-junction structure. This technique is quite powerful since it enables us to fabricate metals along with desired design with complete control. However, it is a high-cost process and rapid fabrications for a wide area (more than cm x cm) is obviously impossible. On the other hand, angular-resolved nanosphere lithography technique also provides a structure of gap-mode LSP [3]. It is a low-cost method and is mainly based on a wet chemical process. It is easy to fabricate an area of cm x cm. However, this method requires highly matured technique and a pretotal procedure is complicated and tasks a long time. Such situation with a lack of user user-friendly techniques to fabricate gap-mode LSP has been a bottle-neck in a development of plasmonics.

In the present study, we propose a user-friendly technique that is with low cost, a total wet process, and a wide-area-treatment. Our method is based on micro-phase separation in a solid film of block-copolymer. Generally, block-copolymers form a sea-island structure in micro-phase separation. Gold nanoparticles (GNPs) are linked to the film only at the island part. These islands are separated by "sea" with a distance of about 100 nm. As a result, when a large part of islands is linked GNPs, GNPs are fixed with being isolated to each other with a distance below 100 nm. That is a gap-mode metallic structure is prepared by a simple manner

of spin-coating, dipping, casting, and drying procedures.



Figure 1 An AFM image of the Au nanoparticles array.



Figure 2 An AFM image of the Au nanoparticles array.

Representative results are shown here. Figure 1 shows a surface morphology of such nanostructures. GNPs are semi-regularly fixed on a glass substrate with a high density. Figure 2 shows optical extinction spectrum of the substrate. We cleary realize a broad and intense band around 750 nm. This is obviously ascribed to a resonant transition of gap-mode LSP. For the substrate, we examined a function to enhance an electromagnetic field. Both in SERS measurements and plasmonic optical trapping, the substrate fabricated here showed a strong enhancement activity based on gap-mode LSP.

In conclusion, the LSP- substrate can be easily prepared and has a high potential in various LSP applications.

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