

Fabrication and evaluation of ring-shaped PS@Au metallodielectric nanoshell arrays

リング型PS@Auプラズモニクナノシェルアレイ作製とその評価

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We have demonstrated the fabrication of two-dimensional periodical non-close packed arrays of sphere-shaped polystyrene(PS)@Au metallodielectric plasmonic nanoshell. The fabrication process of nanoshell arrays is constructed by stepwise integration of colloidal self-assembly of PS nanoparticle monolayer, dry-etching under atmospheric pressure plasma, and surface metallization. Air-plasma treatment, with filament discharge, enabled to fabricate ring shaped PS array from sphere PS nanoparticles by combination of etching and sputter deposition. We succeeded in fabrication of ring-shaped PS@Au nanoparticles array in large area and evaluated the optical property.

1. Introduction

Recently, the localized surface plasmon resonance (LSPR) nanosensor becomes a hot spot due to their unique characteristics. The LSPR-based biosensor has many advantages such as convenience, high sensitivity, wide application, real-time detection, etc. Optical properties of the metal nanoparticles mainly depend on their size, shape, metal composition, and refractive index of the surrounding materials. For use as ultrasensitive detectors of biomolecular, LSPR peak shift with change in refractive index by antigen-antibody reaction is observed, after antibody or antibody fragments are immobilized on the nanoparticles. For biomedical applications that require deeper penetration of near-IR light (800-1200nm) to which both blood and soft tissues are highly transparent, we have thought to fabricate PS@Au metallodielectric nanoshell arrays to make use of plasmon hybridization [2][3]. In this study, we aim at fabrication of ring-shaped PS@Au nanoparticles in large area in order to improve the sensing sensitivity.

2. Experimental Section

Fabrication procedures of ring-shaped nanoshell array consists of four main steps as follows: (1) coating a substrate with ultrathin film of PS as binding layer; (2) deposition of packed spherical PS nanoparticles of monolayer by spin-coat-assisted colloidal self-assembly; (3) atmospheric pressure plasma etching to fabricate non-close-packed periodic array of PS nanoparticles and convert

original sphere-shaped into ring-shaped nanoparticles; (4) Au metalizing by vacuum vapor deposition.

We used commercially available monodisperse PS particles with a diameter of 320 nm whose surface was modified with sulphonic functional group. A densely packed array consisting of a single layer of spherical PS nanoparticles was deposited on a substrate by spin-coating from aqueous solution at a concentration of 10wt%.

Atmospheric pressure air-plasma, which modifies the surface of the PS ultrathin film and fabricates non-close-packed array of ring-shaped PS nanoparticles, was generated by a dielectric barrier discharge (DBD) plasma reactor. The DBD reactor consisted of an aluminum plane-electrode and a copper rod-electrode covered by alumina. The gap between the copper/alumina electrode and sample was adjusted to 0.5mm. We used a bipolar pulse power supply with the frequency of 1 kHz and the pulse width of 5 μ s.

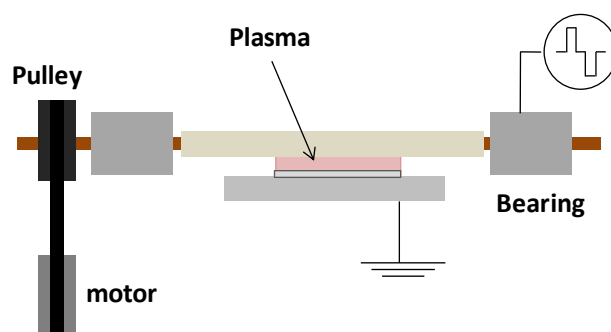


Fig. 1. Schematic diagram of the rotating electrode.

The copper/alumina electrode was rotated to generate uniform plasma along with longitudinal direction of rod electrode. The flow of the air occurred by the rotating electrode and prevented the generation of the discharge locally fixed. The electrode was rotated with a motor, a pulley, a pulley belt, and bearings, and applied the pulse voltage through the bearing (Fig. 1.).

3. Results and Discussion

The DBD generated a gas-phase etching environment which consists of neutrals, electrons, photons, radicals, and positive and negative ions. In the optical emission spectrum obtained from the plasma, the emission spectra of the second positive band of N_2 were obtained but there was no emission spectrum from atomic oxygen under the applied peak voltage of 5kV.

The PS nanoparticles array had been exposed under the DBD air plasma with the filamentary discharge by the bipolar pulse power supply (5kV) to fabricate non-close-packed periodic array. As a result, the PS nanoparticles were etched and the ring-shaped PS nanoparticles were fabricated as shown in Fig. 2.(a). Fig. 1.(b) shows the schematic of preferential etching of the PS nanoparticle and creating of the PS nanoring. The PS nanosphere and

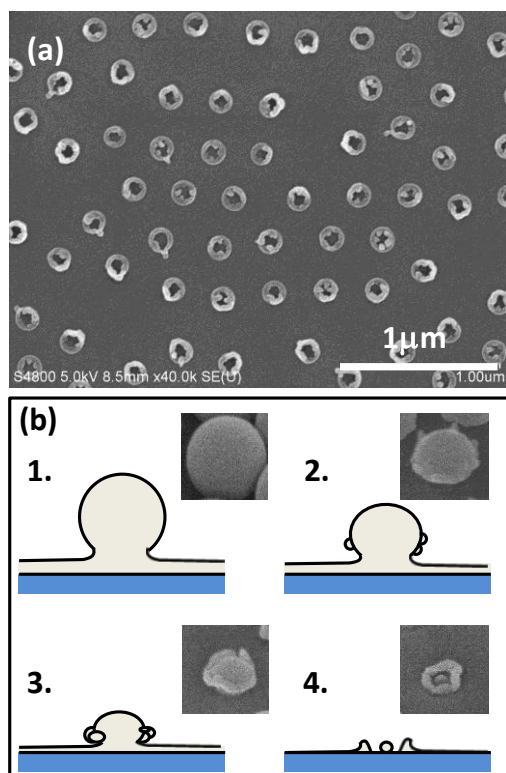


Fig. 2. (a) SEM image of PS nanoring arrays. (b) Schematic illustration of plausible formation mechanism of PS nanoring.

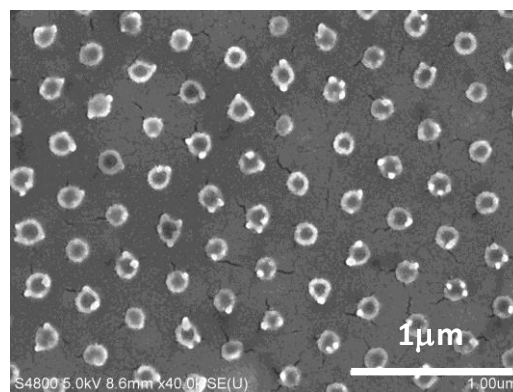


Fig. 3. SEM image of PS@Au nanoring arrays.

the PS ultrathin film were etched by air plasma treatment (b-1). The isotropic PS nanospheres were transformed into the anisotropic shape because the plasma treatment preferentially etched the top of PS nanoparticles and the different curvature was observed between the top and the bottom of nanoparticles (b-2). The plasma was also used to remove the PS ultrathin film. During the etching, the secondary sputtering created the deposition around the base of the nanoparticle (b-3). As the etching progressed, the deposited particles grew larger because of the sputtering from PS film whereas the PS nanoparticle was etched smaller. Finally, the ring-shaped PS nanoparticle remained on the substrate (b-4).

Fig. 3. shows SEM image of nanorings array after metalizing of PS nanoparticles surface by using thermal deposition. Their surface plasmonic properties were evaluated by UV-vis-near-IR spectroscopy, and a plasmon peak at 797nm was observed. The peak came from the structure of ring-shaped PS arrays, because the peak was not observed without the nanoring arrays.

4. Conclusions

Discrete PS nanoring arrays with monolayer were successively fabricated by the DBD air plasma etching. The ring-shaped PS@Au nanoparticles were fabricated by deposition of Au thin film on PS nanorings. The plasmon peak appeared in near infrared. The Au film is deposited on the substrate by thermal vapor deposition. Only PS particles surface will be metalized by plating.

References

- [1] E. Prodan, C. Radloff, N. J. Halas, *Science* **302**, (2003)409.
- [2] S. Uchida, K. Yamamura, N. Zettsu, *Thin Solid Films* **518**, (2010) 3581.
- [3] S. Uchida, K. Yamamura, N. Zettsu, *J. Nanosci. Nanotechnol.* **11**, (2011) 2956.