Plasmonic Growth of Patterned Silver Nanostructures with Fractal Geometry

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1. Introduction

Bulky metallic materials known as metamaterials, that are composed of subwavelength units of plasmonic metallic nanostructures, have been one of the hottest topics in photonics due to their exotic optical properties. However, the fabrication of complex metallic nanostructures in large scale in 3D is still under the development. Most of exciting demonstrations of exotic optical properties by metamaterials have been shown with thin or 2D structures, rather than thick bulky metamaterials, except a few examples such as 3D array of sprit ring resonators in microwave region.

To fabricate metamaterials in optical frequency region, the available nanotechnology is mostly based on silicon fabrication technology. For extending the dimensions into 3D as metamaterials, 2D-layer stacking method has been such as a multi-layered resonator array and a layered fishnet. Two-photon laser drawing is another method for realizing real 3D nano-fabrication. We have fabricated 3D spring array by electroless metal plating on two-photon polymerized microsprings [1]. An array of square-pyramid frames without polymer has been also drawn with two-photon photo-reduction [2]. Two-photon drawing is useful for fabricating arbitrary 3D plasmonic structures in three dimensions, while it takes an extremely long time for fabricating a large object in 3D.

We show a bottom-up approach for producing 3D silver nanostructures in a large scale [3]. Bottom-up approach is more advantageous for building up or self-growing a large-scale complex nanostructures in 3D. Self-assembling of metallic nanoparticles has been studied by other groups where the nanoparticles are used as building-blocks. The silver nanostructures we grow can be as large as possible but with fine details.

2. Fabrication

First, we coat a glass substrate with amino-propyl trimethoxisilane (APTMS) monolayer. Silver nano-seeds of a few to several nm in diameter, stabilized by citric acid, are fixed on the APTMS-coated glass substrate. Then, we remove the APTMS, which is hydrophilic by UV ozone cleaning. APTMS is replaced by dimethyldichlorosilane, which exhibits hydrophobicity. Then the silver ion solution is dropped onto it. The solution is composed of acetone-water solution of silver nitrate and L-ascorbic acid. The experimental parameters, temperature, surface tension, and viscosity of solvent, are optimized to produce fractal geometries of structures. Next, the substrate with the silver solution droplet is illuminated with a UV laser (355 nm), which is close enough to the plasmonic resonant peak of the silver nano-seeds.

3. Results and Discussions

Massive silver nano-trees are grown through needle growing and branching of silver nanocrystals. Fig. 1 shows a silver forest as large as 1.2×1.2 mm^2. It looks as a Chinese character of “tree” according the mask pattern for illumination as shown in the left part of Fig. 1. The middle part of Fig. 1 is an enlarged view of the central area of the “tree” with magnification of ×800, showing massive nano-trees similar to a forest. The right image shows further enlargement of the image in the middle with magnification of ×8,000, showing tree-like structures made of silver, typically with a length of a few tens of μm, with branches of a few μm and leaves of a few tens of nm.

We analyzed the fractal geometry of the silver nano-trees, and applied the silver nano-forests to surface-enhanced Raman sensing, which are also shown in the presentation.

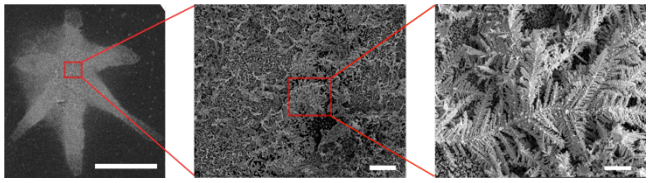

Fig. 1 SEM images of silver nano-trees grown on an area patterned after the Chinese character of “tree”. The scale bar is 500 μm (left), 20 μm (middle) and 2 μm (right).

3. Conclusions

We have developed a self-growing method of metallic metamaterials with self-similarity. An application of the developed structures was shown through experiments of surface-enhanced Raman sensing of molecules with large enhancement due to its fractal nature.

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