Gold nanostructures for optical metamaterials using genetically modified tobacco mosaic virus

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Abstract

We report here the fabrication of gold nanostructures using genetically modified tobacco mosaic virus (TMV) as a template. 5-nm gold nanoparticles with small standard deviation in size are formed on the TMV fused with titanium (Ti) binding peptide, leading to realization of 3D optical metamaterials.

1. Introduction

The demonstration by Smith and co-workers [1, 2] of metamaterials that have a negative index of refraction using millimeter-sized metallic copper strips and split-ring resonators operating at microwave frequencies sparked a considerable amount of research activities to scale down the size of meta-atoms and meta-molecules for the purpose of realizing metamaterials operating at higher frequencies. In resonant element-based metamaterials operating at optical frequencies, e.g., visible light with wavelength of several hundred nanometers, meta-atoms need to be several tens of nanometer in size.[3] In addition, the meta-molecule consisting of meta-atoms need to be constructed in three dimensions (3D) to generate significant scattering.[4] Fabrication of meta-molecules that operate at optical frequencies are, however, still a challenge even for the state-of-the-art nano-fabrication techniques.

We report here the alignment of gold nanoparticles in 3D around tobacco mosaic virus (TMV) as a template. We showed that 5-nm gold nanoparticles with small standard deviation in size are formed on genetically modified TMV with titanium binding peptide, leading to 3D nanostructures. The uniform structure is essential for monochromatic optical resonators. Our results open a new avenue for the preparation of meta-molecules and metamaterials in optical frequencies.

2. Experimental

TMV is a tube-shaped plant virus 300 nm in length with outer- and inner-diameter of 18 nm and 4 nm, respectively. The virion consists of a helical single-strand ribonucleic acid (RNA) surrounded by 2130 coat proteins. The surface of the TMV shows a helical structure representing the helical RNA. The helical structure of the virus is an attracting feature to be used as a template for chiral metamaterials.

To facilitate preferred mineralization ability to TMV, we genetically fused material-binding peptides to the outer-surface of the virus. Previously, a number of material-binding peptides have been reported to be able to promote metal crystallization. In this study, we fused a gold-binding peptide (GBP) to TMV (GBP-TMV)[5] or a titanium-binding peptide (TBP) to TMV (TBP-TMV).[6]

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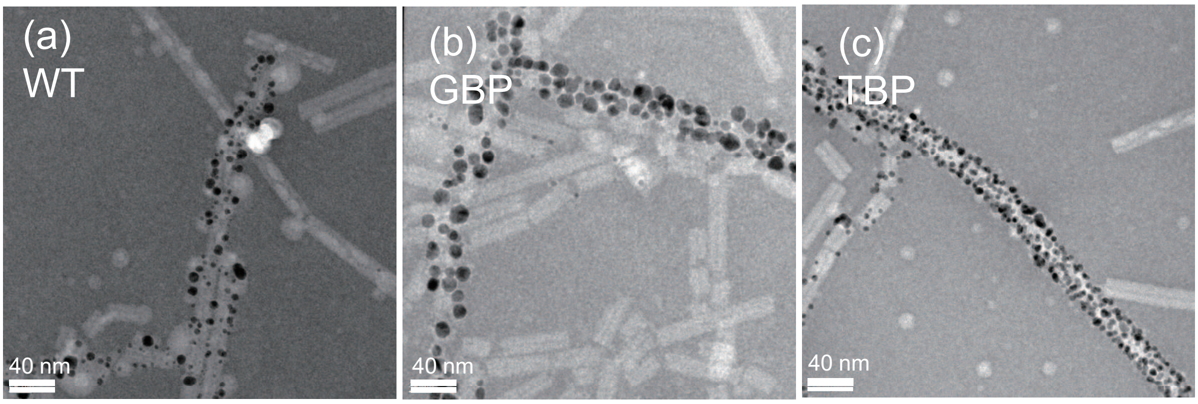

Fig. 1: TEM images of (a) wild-type TMV, (b) GBP-TMV, and (c) TBP-TMV after gold deposition.

A plasmid encoding the genomic sequence of TMV was used as a parent plasmid. Genomic RNA of the mutant were synthesized in vitro, and tobacco plant (Nicotiana benthamiana) was infected. After one week, leaves were harvested and virion was purified as previously described.[7] Although not shown here, TEM image show the tube shape of GBP-TMV and TBP-TMV very similar to the wild-type. For gold deposition, wild-type TMV, GBP-TMV, or TBP-TMV was mixed with $KAuCl_4$ in the presence of 5% acetic acid, and the solution was reduced by 5 mM $NaBH_4$ for 20 min at room temperature.[8]

3. Results and Discussion

Figure 1(a) shows a TEM image of wild-type TMV after gold deposition. White rods correspond to TMV virion. Black patches attached to the virion correspond to gold nanoparticles. We see that gold nanoparticles are randomly deposited on the TMV. Figure 1(b) shows a TEM image of GBP-TMV after gold deposition. The size of gold nanoparticles deposited was much larger than that obtained by using wild-type TMV. The diameter of gold nanoparticles on GBP-TMV was 10.12 ± 2.53 nm while that on wild-type TMV was 4.78 ± 2.18 nm. These results suggest that the gold deposition using GBP-TMV was promoted as compared to wild-type TMV.

Figure 1(c) shows a TEM image of TBP-TMV after gold deposition. Surprisingly, with TBP-TMV mutant, small gold nanoparticles with low standard deviation could be formed on the outer-surface of the virion. The diameter of gold nanoparticles on TBP-TMV was 4.96 ± 1.06 nm. The diameter of gold nanoparticles was larger when 10-fold $KAuCl_4$ concentration was used for TBP-TMV mineralization (9.25 ± 1.84nm) although not shown here.

TEM studies showed that GBP-TMV promotes the growth of gold nanoparticles on the virion. However, the particle size is not uniform. On the other hand, gold deposition using TBP-TMV results in formation of gold nanoparticles with uniform size. This indicates that the number of nucleation sites increases on TBP-TMV. Before reduction, gold ions are absorbed in TMV coat proteins. The reduction is carried out on the surface of the virion. The number of TBP on one virion tube is, however, much smaller than that of gold nanoparticles segregated. This rules out the possibility of TBP on TMV as the nucleation cites. It is thus plausible that a display of TBP alters the electric charge balance on TMV. The change promotes the nucleation of gold nanoparticles.

Plasmonic properties of the samples were verified using ultraviolet-visible (UV-Vis.) transmission spectroscopy. The UV-Vis. spectra of gold-deposited wild-type-, GBP-, and TBP-TMV show an absorption peak around 550 nm, corresponding to localized surface plasmon of gold nanoparticles in acetic acid (not shown here). To realize truly three dimensional structures, the alignment of the gold-mineralized TMV is necessary. We think that the alignment can be achieved by using a substrate with small holes. The micro-fabrication of small holes on a silicon substrate is now underway in our group.

4. Conclusion

A TMV surrounded by gold nanoparticles was fabricated. By using TBP-TMV, the diameter of nanoparticles was 5 nm with standard deviation of about 1 nm, which is smaller than those deposited on wild-type TMV. GBP-TMV brings about the formation of larger gold nanoparticles around 10 nm in diameter. Even though it is still difficult to control the place of gold deposited on the virion, genetically-modified TMV is a promising template for construction for optical metamaterials.

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