Chiral meta-molecules composed of gold nanoparticles and tobacco mosaic virus

S. Tomita[1], M. Kobayashi[2], K. Sawada[3], K. Shiba[2], H. Yanagi[1], I. Yamashita[1], Y. Uraoka[1]

[1]Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama, Ikoma, Nara 630-0192, Japan
Fax: +81-743-72-6015; email: tomita@ms.naist.jp
[2]Division of Protein Engineering, The Cancer Institute of the Japanese Foundation for Cancer Research (JFCR), 3-8-31 Ariake, Koto, Tokyo 135-8550, Japan
[3]RIKEN, SPring-8 Center, 1-1-1 Kouto, Sayo, Hyogo 679-5148, Japan

Abstract

We report a chiral meta-molecule in the ultra-violet (UV) and visible (VIS) regions using a complex of Au nanoparticles and rod-shaped tobacco mosaic virus (TMV). A complex of Au nanoparticles five nm in diameter and peptide-modified TMV shows a negative circular dichroism (CD) peak at plasmonic resonance wavelength around 540 nm of Au nanoparticles. Additionally, modification of a CD peak in the UV region is observed. A theoretical consideration suggests that attaching nanoparticles to virus causes the enhancement and modification of CD peaks in both the UV and VIS region. Our results open a new avenue for the preparation of 3D chiral meta-materials in optical frequencies.

1. Introduction

Chiral metamaterials [1] are of great interest because they realize negative refraction of light even without a negative index of refraction.[2] When considering chiral metamaterials operating at optical frequencies, one may utilize plasmonic metal, for example, gold (Au) nanoparticles several tens of nanometers in diameter owing to their strong interaction with visible (VIS) light. The plasmonic nanoparticles do not, however, show optical activity in the VIS region. Asymmetric plasmonic nanostructures fabricated by electron beam lithography was thus necessary to introduce chirality.[3, 4] The formation of a complex with chiral molecules is another way to give an optical activity to plasmonic nanoparticles in the VIS region.[5, 6] In this contribution, we report a chiral meta-molecule in the optical region made of Au nanoparticles and tobacco mosaic virus (TMV).

2. Experimental procedures

TMV is a rod-shaped plant virus consisting of a right-handed helical single-strand ribonucleic acid (RNA) surrounded by 2130 coat proteins. We genetically fused a titanium-binding peptide (TBP; Arg-Lys-Leu-Pro-Asp-Ala)[7], which has been shown to promote mineralization of a plasmonic metal[8], to the outer-surface of the virus. We call this engineered virus TBP-TMV. The detailed construction procedures of plasmids encoding TBP-TMV, and preparation and purification of the virus has been described elsewhere.[9] For Au deposition, wild-type TMV (WT-TMV, ToMV species) or TBP-TMV was mixed with potassium chloroaurate ($KAuCl_4$) in the presence of 5% acetic acid, and the solution was reduced by 5 mM sodium borohydride ($NaBH_4$) for 20 min at ambient conditions. CD and absorption spectra between 200 and 700 nm of the dried samples were simultaneously measured using a spectropolarimeter (JASCO J-820).

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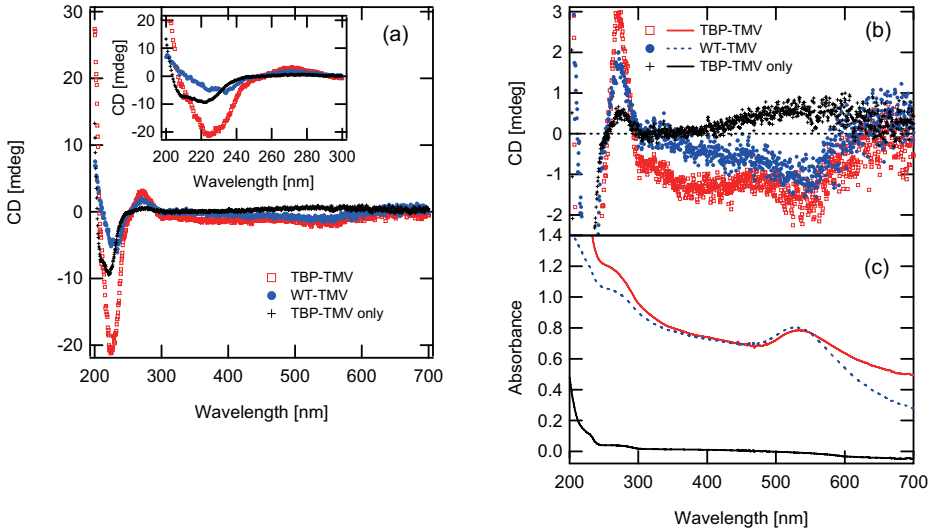

Fig. 1: (a) CD spectra of the complexes of Au nanoparticles with TBP-TMV (red open squares) and WT-TMV (blue filled circles). Black crosses corresponds to TBP-TMV only. The inset shows enlarged spectra between 200 and 300 nm. (b) CD spectra same as (a), but enlarged between CD = +3 and -3 mdeg. (c) Simultaneously measured UV-VIS spectra of the complexes.

3. Results and discussion

Fig. 1(a) shows CD spectra of the TMV-Au complexes. Strong CD bands are observed in the UV region. Enlarged CD spectra between 200 and 300 nm are shown as the inset. It is known that right-handed α-helices, which consist of amino acids, in TMV coat proteins show a positive CD peak at 190 nm and a negative peak at 209 nm deriving from the excitation of π to π* transition with optical dipoles perpendicular and parallel to the axis, respectively.[10] The α-helix also shows a negative CD peak at 222 nm owing to the n to π* transition with parallel dipole. In addition to these peaks, a positive CD peak around 280 nm is known to be attributed to aromatic residues of the coat protein. These peaks are observed for TBP-TMV without Au nanoparticles as shown by black crosses in Fig. 1(a). It should be stressed that the TMV-Au complexes show different band shapes. Particularly for the complex with TBP-TMV, the negative CD peak at 222 nm is significantly enhanced compared to the negative peak at 209 nm.

Fig. 1(b) shows CD spectra same as (a), but enlarged between CD = +3 and -3 mdeg. TBP-TMV only (without Au nanoparticles) shows no obvious CD peak in the region between 300 nm and 700 nm. Contrastingly, a negative CD peak in plasmon wavelength around 540 nm was observed for the complex with TBP-TMV even though optical activity in this region is negligible for TMV or Au nanoparticles themselves. A similar negative CD peak was observed for a complex with WT-TMV. It is noteworthy that the absorption peak derived from localized surface plasmon of Au nanoparticles was also observed around 540 nm (Fig. 1(c)). This indicates the interaction of plasmonic resonance and optical activity. It should be reminded here that a CD band between 200 and 300 nm also changed the shape and the negative peak at 222 nm was enhanced after the formation of Au nanoparticles, particularly when using TBP-TMV. By attaching Au nanoparticles to TMV, optical activity enhanced at two different wavelength.

In the present experiments, the CD peaks are originated from the chiral structures in the complex of TMV and Au nanoparticles. In the complex, there are two types of chiral structures: right-handed amino acids, right-handed α-helices consisted of amino acids. We thus consider TMV as a chiral medium, in which the indices of refraction for right-handed and left-handed polarizations propagating toward $+x$-direction are n_+, n_-, respectively. The refractive indices depends on propagating directions: a right- (left-) handed polarized light toward $-x$-direction feels n_- (n_+). Such a directional difference of the

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indices of refraction plays an essential role in our results. We suppose that the chiral medium is connected to a normal medium with the refractive index, n. The length of the normal and chiral medium is l and $L-l$, respectively. The ratio of transmission coefficient for right-handed polarization t_+ and left-handed polarization t_- is calculated by a transfer matrix method. The ratio t_-/t_+ is expressed as

$$\frac{t_-}{t_+} = e^{-2i(\theta_+ - \theta_-)} \times \frac{A_{+-}}{A_{-+}}, \tag{1}$$

where

$$\begin{aligned} A_{+-} &= (\cos\theta - \frac{i}{n}\sin\theta) \\ &\times \left[n_+ e^{i\alpha_{+-}} + n_- e^{-i\alpha_{-+}} + n_+ n_- (e^{i\alpha_{+-}} - e^{-i\alpha_{-+}})\right] \\ &+ (\cos\theta - ni\sin\theta) \\ &\times (e^{i\alpha_{+-}} - e^{i\alpha_{-+}} + n_- e^{i\alpha_{+-}} + n_+ e^{-i\alpha_{-+}}), \end{aligned}$$

with $\theta = kl/n$, $\theta_{+,-} = kl/n_{+,-}$ and $\alpha_{+-} = kl/n_+ - kL/n_-$.

The first factor of right-hand side of Eq. (1), $e^{-2i(\theta_+ - \theta_-)}$, gives the optical activity without the normal medium. The second factor, A_{+-}/A_{-+}, corresponds to the effect of attaching normal to chiral medium in optical activity. $A_{+-}/A_{-+} \neq 1$ means modification of the optical activity. In plasmon frequency, A_{+-}/A_{-+} is significantly large due to the plasmon resonance, leading to the significant enhancement of optical activity. On the other hand, in UV region, $A_{+-}/A_{-+} \simeq 1$. This should enhance the optical activity of the complex; the optical activity of the complex in UV region is not smaller than that of the chiral medium alone. This simple model provides a consistent explanation to the present experimental results.

4. Conclusion

In conclusion, we succeeded in fabricating an optically active chiral meta-molecule in the UV and VIS regions utilizing a TMV and Au nanoparticles. A plasmon-induced CD effect is observed in the VIS region. Moreover, CD signals in the UV region caused by the amino acids is also modified. A theoretical scheme demonstrated that attaching nanoparticle to protein causes the enhancement and modification of CD peaks both in the UV and VIS regions. The well-defined complex of Au nanoparticles and an engineered TMV constructed in this study is thus a promising building block for 3D optical chiral meta-materials.

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