様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

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研究課題名（和文）Amplification of Chiral Light-Matter Interaction Using Bottom-Up 3D Chiral Nanoparticle

研究課題名（英文）Amplification of Chiral Light-Matter Interaction Using Bottom-Up 3D Chiral Nanoparticle

研究代表者

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交付決定額（研究期間全体）：（直接経費）　　1,600,000円

研究成果の概要（和文）：この研究プロジェクトの主な目的は、ボトムアップベースの3Dキラルナノ粒子をメディエーターとして使用して、キラルな光と物質の相互作用を増幅する方法を開発することです。 従来の化学合成法には、鏡面対称性を自発的に破ってキラル構造を作ることが難しいという弱点があります。 この研究は、キラルナノ粒子の新規合成とプラズモンナノ構造の局所電磁場のキラリティーの詳細な分析に基づいて、これらの制限を克服しようとしました。 研究期間中、1）プラズモンヘリコイドナノ粒子の強いキロプチカル信号の生成メカニズムの調査、2）キラルナノ粒子と分子間のナノスケール結合の調査に成功しました。

研究成果の学術的意義や社会的意義
私たちの研究は、キラルな光と物質の相互作用を強力に強化できる新しいボトムアップベースのプラットフォームを実証することに成功しました。 この研究は、キラル光と物質の相互作用の基本的な理解に非常に役立つだけでなく、キラルセンシング、偏光選択デバイス、量子通信、 と暗号化。 この研究が将来の医療アプリケーションと情報技術に貢献することを期待しています。

研究成果の概要（英文）：The major purpose of this research project is to develop a method for amplifying chiral light-matter interactions using bottom-up-based 3D chiral nanoparticles as mediators. Conventional chemical synthesis methods have an unavoidable weakness in that it is difficult to spontaneously break mirror symmetry and make chiral structures, and the diversity of structures that can be obtained is limited. This study attempted to overcome these limitations based on the recent advance of chiral nanoparticle synthesis using a chirality transfer mechanism and in-depth analysis on the chirality of the local electromagnetic field of the plasmonic nanostructure. During the research period, we succeeded in 1) investigation a mechanism for the generation of a strong chiroptical signal of the plasmonic helicoid nanoparticle and 2) nanoscale coupling between chiral nanoparticles and molecules.

研究分野：Chiral nanomaterial

キーワード：chiral　plasmon　nearfield　nanoparticle　biomolecule

１．研究開始当初の背景

Investigating the chirality of matter and its related phenomena has been a central part of understanding various asymmetric physical and chemical phenomena in natural organisms, catalysis reaction, light polarization, and electronic spins. In particular, the light-matter interaction of chiral material is directly related to its three-dimensional geometry and has been adopted to probe the structural changes at the molecular level. For example, polarization-based "chiroptical" spectroscopy, such as circular dichroism (CD), has been used for the investigation of biomolecular structures. However, since the chiroptical signals originating from the molecules are 10^{-6} to 10^{-2} times smaller than its absorption, detection of the chiroptical signal itself from the tiny amount of target molecule is extremely difficult. Therefore, a method for amplifying chiral light-matter interactions is required for the ultrasensitive measurement of chiroptical signal.

In order to improve this situation, chiral plasmonic nanostructure can be adopted to enhance the chiroptical signal of the molecule. The key role of the chiral plasmonic nanostructure is to generate a “chiral hotspot” by twisting the light energy and phase locally around the nanostructure. Theoretical [Cohen et al., PRL 104, 163901 (2010)] and experimental [Kadodwala et al., Nat. Nanotech. 5, 783–787 (2010)] studies have already demonstrated that the chiral light-matter interaction can be locally controlled to amplify the originally weak chiroptical signal. However, the most important but still challenging part of this research is to efficiently generate chiral structure in nanoscale and to maximize the chiroptical effect of desired handedness.

２．研究の目的

We focused on the possibility to manipulate the chirality of light in the nanometer level using the bottom-up synthesis technology of colloidal metal nanoparticles. Conventional chemical synthesis methods have an unavoidable weakness in that it is difficult to spontaneously break mirror symmetry and make chiral structures, and the diversity of structures that can be obtained is limited. This study attempted to overcome these limitations based on the recent advance of chiral nanoparticle synthesis using chirality transfer mechanism and in-depth analysis on the chirality of local electromagnetic field of the plasmonic nanostructure. During the research period, we aimed on (1) Investigation of a mechanism for the generation of a strong chiroptical signal of the plasmonic helicoid nanoparticle and (2) Nanoscale coupling between chiral nanoparticles and molecules.

３．研究の方法

(1) Investigation of a mechanism for the generation of a strong chiroptical signal of the plasmonic helicoid nanoparticle

Plasmonic metal nanostructure can dynamically control the light-matter interaction due to the localized photonic environment near the surface such as significant enhancement of intensity, phase delay, and chirality of electromagnetic fields. Our gold “helicoid” nanoparticle, synthesized under the enantioselective interaction between peptide and metal surface [Ahn et al., Nature 556, 360 (2018)], can be an efficient platform to generate and amplify the chiroptical response due to its highly twisted chiral nanostructure. In order to prove this capability, we demonstrated strong chirality of local electromagnetic field using scanning near-field microscopy technique and finite-difference time domain (FDTD) simulation.

As an effort to investigate the enhancement effect of this local chiral field, we designed two-photon-induced photoluminescence (TPI-PL) experiment using the gold helicoid nanoparticle (Fig. 1). Without using any secondary emitters, the gold nanoparticle can produced a broad emission in a visible wavelength range (λ>400nm) due to the two-photon-induced interband absorption and subsequent radiative recombination of intrinsic gold material. This intrinsic emission of gold, which is basically achiral, could be modulated by the influence of the local electromagnetic field which has strong intensity and chirality. To evaluate the chiroptical response, we carefully analyzed the polarization state of emitted light.

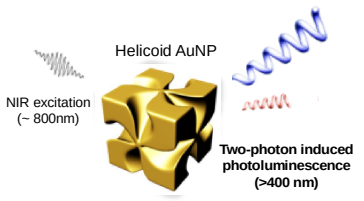

Fig 1. Chiral Two-photon-induced photoluminescence of gold helicoid nanoparticle.

(2) Nanoscale coupling between chiral nanoparticles and molecules.

The coupling of molecular targets with a confined field created by plasmonic nanostructure can strongly affect the optical response of the original molecule, such as significant enhancement of intensity, phase delay, and local chirality. We studied the chiroptical property of molecule−nanoparticle coupled system using chiral helicoid gold nanoparticles. Using a gold helicoid nanoparticle as a host, a dye molecule was conjugated on the surface of the nanoparticle. To prove the strong chiral light-matter interaction of gold

helicoid nanoparticle, we used a dye molecule with achiral molecular structure which showed no chiroptical responses by itself. Using the coupled system of achiral dye and gold helicoid nanoparticle, we evaluated circular polarization state of emitted light.

In addition to the gold helicoid nanoparticle, we developed chiral coupling method using even achiral nanostructure. We used anisotropic nanostructure, such as rectangle, as a host of strong chiral light-matter interaction. Although the overall response averages to zero due to the structure is achiral, our previous researches [ACS Photonics 2018, 5, 4, 1486–1492] and recent numerical simulation (Fig. 2) reveal that this anisotropic structure provide an exceptionally large contrast between left circular polarization (LCP) and right circular polarization (RCP) mode in a local area (Fig. 2a,b). Based on this knowledge, we adopted plasmon-induced localized photochemical reaction to realize a precise light-matter coupling in the chiral hotspot.

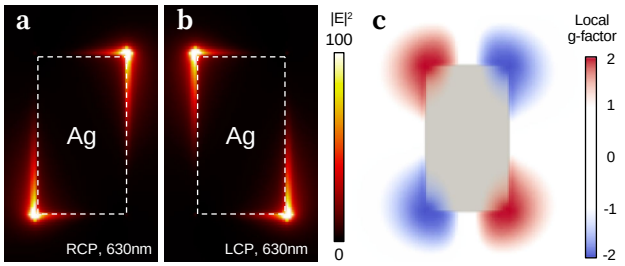

Fig 2. (a,b) Plasmon mode of nanocuboid under RCP (a) and LCP (b) excitation. (c) Corresponding local g-factor distribution showing chiral hotspots.

4．研究成果

(1) Investigation of a mechanism for the generation of a strong chiroptical signal of the plasmonic helicoid nanoparticle

To evaluate the chiroptical property of gold helicoid nanoparticle, we utilized the nearfield polarimetry technique [ACS Photonics 2018, 5, 4, 1486–1492] which can measure the local contrast of LCP and RCP field intensity at 10 ~ 50 nm resolution. According to the nearfield polarimetry measurement, the gold helicoid nanoparticle showed strong chirality of electromagnetic field, as indicated in Fig. 3a. This result was also proved in the finite difference time domain (FDTD) simulation (Fig. 3b), which shows that the chiral hotspot was generated at the chiral gap structures on the particle surface.

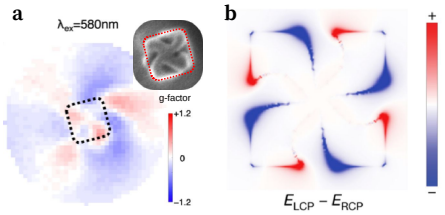

Fig 3. (a) Nearfield polarimetry measurement of single helicoid nanoparticle. (b) Difference of electric field distribution between LCP and RCP mode.

Based on this chiral hotspot of local electromagnetic field, we succeeded to observe the generation of high-purity circularly polarized light from the intrinsic emission of gold nanoparticles. TPI-PL imaging (Fig. 4b,c) and spectroscopy (Fig. 4d) on a single particle clearly show that the polarization state of emission was strongly biased to RCP with the g-factor of ~1.1 at 638nm (Fig. 4e). A survey on fifteen different chiral particles reveals that a maximum and average g-factor was about 1.4 and 0.7, while the achiral (cubic) nanoparticle has no chiroptical response. To the best of our knowledge, the g-factor observed in this research is one of the highest records of circularly polarized emission using chiral plasmonic nanoparticle.

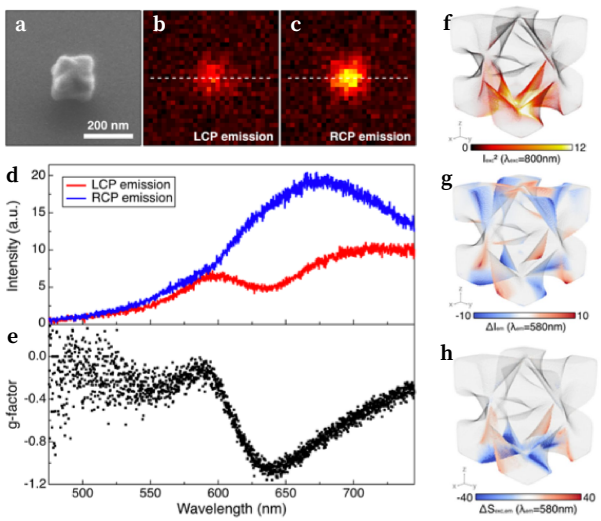

Fig 4. (a) SEM image and (b,c) TPI-PL mapping for LCP (b) and RCP (c) emission of a single helicoid nanoparticle. (d,e) TPI-PL (d) and corresponding luminescence g-factor (e) spectra of a single helicoid nanoparticle. (f,g) Local field distribution at excitation (f) and emission (g) wavelengths. (h) Overlap of excitation and emission field distribution.

The physical origin of the strong chiral light emission was also studied. Our numerical simulation clearly shows that 1) local confinement of excitation mode which is mainly active on the bottom-side chiral nanogap structure (Fig. 4f), 2) contrast between LCP and RCP plasmonic mode at emission wavelength (Fig. 4g), and 3) strong dissymmetry of spatial overlap of these excitation and emission mode biased to RCP emission (Fig. 4h). This analysis well explains the exceptional performance of chiral light emission that occurs in the gold helicoid nanoparticle.

(2) Nanoscale coupling between chiral nanoparticles and molecules.

The coupling of gold helicoid nanoparticle and dye molecule was achieved by the simple spin-coating method (Fig. 5a). Rhodamine 6G was used as a dye molecule, which has an achiral molecular structure with excitation and emission wavelength of 532 nm and 560 nm. To evaluate the chiroptical response, we measured the polarization state of emitted light of this hybrid system. Because of its achiral structure, original rhodamine 6G shows no difference between RCP and LCP emission (Fig. 5b, dotted curve). On the other hand, the coupling of rhodamine 6G and gold helicoid nanoparticles results in strong chiral light emission, which was biased to RCP with the g-factor of ~0.3 at 560nm (Fig. 5b, solid curve). This result suggests that the chirality of the local electromagnetic field can be effectively transferred to nearby molecules, regardless of the intrinsic chirality of the molecule itself. We expect that this technique can provide an effective route for the amplification of chiral light-matter interaction.

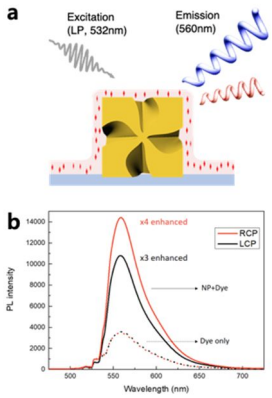

Fig 5. (a) Shematics and (b) PL spectrum of nanoparticle-dye hybrid.

In addition, a method for utilizing a chiral hot-spot based on the anisotropic nanoparticle was developed. Using the chiroptical photopolymerization approach on the surface of plasmonic nanocuboid particles, we succeeded to produce a chiral hybrid nanostructure that accurately coupled molecular dye and chiral hot-spots. Due to the large contrast between LCP and RCP mode in rectangular geometry, the local photopolymerization reaction under the exposure of circularly polarized light selectively produces left- and right-handed nanohybrid structures (Fig. 6a). The fabricated chiral nanohybrid structure showed a strong circular dichroism response in the visible wavelength (Fig. 6b,c). The polymer layer formed on the surface of the nanoparticle not only created chiral geometries but served as a matrix for the chiral light-matter coupling by embedding secondary materials inside. For example, we succeeded to produce a dye-embedded polymer structure that places organic dye molecules into the chiral hotspot region (Fig. 6d). We believe that this approach can provide a reproducible method for the nanoscale control of chiral hotspots and their coupling to target molecules.

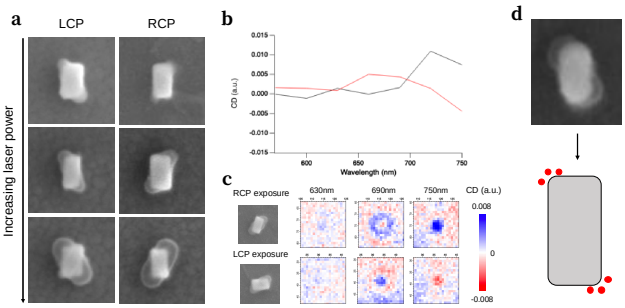

Fig 6. (a) Chiral nanohybrid structure produced by plasmon-induced photopolymerization reaction with LCP and RCP illumination. (b) CD spectra and (c) far-field CD imaging of left- and right-handed chiral nanohybrid. (d) Chiral nanohybrid embedding 1 wt% of tetraphenylporphyrin dye molecule.

５．主な発表論文等

〔雑誌論文〕　計0件

〔学会発表〕　計3件（うち招待講演　0件／うち国際学会　3件）

１．発表者名 Hyo-Yong Ahn
２．発表標題 Singular Chiroplasmonic Nanoparticle for Strong Optical Activity
３．学会等名 The International Symposium on Plasmonics and Nano-photonics (iSPN2019)（国際学会）
４．発表年 2019年

１．発表者名 Hyo-Yong Ahn
２．発表標題 Peptide-Derived Nanoscale Chirality of FCC Metal for Strong Optical Activity
３．学会等名 International Symposium on Circularly Polarized Luminescence and the Related Phenomena (ISCPL 2019)（国際学会）
４．発表年 2019年

１．発表者名 Hyo-Yong Ahn
２．発表標題 Plasmonic Chiroptical Responses of 3D Continuous Chiral Nanoparticles
３．学会等名 Materials Research Meeting 2019（国際学会）
４．発表年 2019年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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6．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

7．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

8．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関