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研究課題名(和文)多孔性錯体/金属ナノ結晶ハイブリッド材料による光応答型生体活性分子放出

研究課題名(英文) Creation of new molecular release systems based on porous coordination polymer capable and metal nanoparticles capable of remotely deliver biologically active molecules under light irradiation

研究代表者

Reboul Julien (Reboul, Julien)

京都大学・物質-細胞統合システム拠点・助教

研究者番号：20604747

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研究成果の概要(和文)：本研究では、光刺激により生体活性分子を放出する新しい分子放出システムを開発した。有機分子と金属イオンによって組み上がる多孔性金属錯体は、その孔の中に大量の分子を貯蔵することができる結晶である。この結晶と光熱変換可能な金ナノロッドを融合することで新しいメソスコピックコンポジットの合成を行った。発光特性を持つアントラセンをプローブ分子として多孔性金属錯体中に貯蔵しておき、光刺激による分子放出制御を蛍光スペクトルにより検出することに成功した。これにより、様々な分子を多孔性金属錯体に閉じ込め、必要な時に取り出すことが可能なシステムの構築に成功した。

研究成果の概要(英文)：We created new molecular release systems capable of remotely deliver biologically active molecules under light irradiation. To this end, we combined the high storage ability of porous coordination polymers (PCPs), a new class of crystalline materials assembled by organic linkers and inorganic joints at the molecular scale, with the photo-thermal properties of gold nanorods (GNRs) into designed mesoscopic composite materials. These materials consisted in core shell structures composed of a GNR core and an aluminum-based PCP shell. The creation of such mesoscopic structures enabled the implementation of unique motion-induced molecular release, triggered by the highly efficient conversion of optical energy into heat that occurs when the GNRs are irradiated into their plasmon band. Temporal control of the molecular release was demonstrated with anthracene as a guest molecule (priorly immobilized within the pores of the PCP shell) and fluorescent probe by fluorescence spectroscopy.

研究分野：化学

科研費の分科・細目：材料化学・無機工業材料

キーワード：多孔性金属錯体 金属ナノ粒子 分子放出制御 生体活性分子 細胞機能評価

1. 研究開始当初の背景

Controlled release of chemical substances has proved to be useful in a number of areas including food, pesticide, cosmetic, or medicine. In contrast to spontaneous release system from which molecules simply leak, the sophisticated design of materials is required for the development of a controlled or switchable system, in which the release can be initiated or interrupted by responding to external environmental changes, such as temperature, pH, magnetic or electric fields, and ultrasound. In particular, light as an external stimulus is certainly promising because of its facile localizability toward the control of molecular release in spatial and temporal fashions.

2. 研究の目的

Porous coordination polymers (PCPs), a class of crystalline microporous materials composed of metal ions connected to each other by organic ligands, are good candidates for host matrices that transitory but effectively store molecules. This is because of the designability of pores in uniform size and in surface nature for the tunable framework-guest interaction. Noteworthy, the research on PCPs is totally focused on the control of in-coming molecules into the pores to develop materials for applications in storage, separation, catalysis and sensing. Regarding the releasing property, only few studies in which the releasing can be initiated by exposing the materials to certain environmental conditions were reported so far. Also, the interruption and restarting of molecular release in a controlled manner has never been achieved with this new class of porous material.

The goal of our study was to exploit the outstanding porous properties as well as the molecular stabilization ability of PCPs to fabricate a novel generation of hybrid devices that temporally controls the release of molecules by light irradiation.

3. 研究の方法

To reach our goal, our idea was to combine the high storage ability of PCPs with the photo-thermal properties of gold nanorods (GNRs) into designed mesoscopic composite nanomaterials, for which the core-shell structures was composed of an individual GNR core and an aluminum-based PCP shell. This core-shell configuration enabled us to efficiently exploit the plasmonic

effect of gold nanorods. Upon near infrared (NIR) light irradiation into the plasmon bands of GNRs, electrons at the excited conduction band relax to the ground state, simultaneously dissipating the resulting excess energy by the conversion of optical energy to heat. In our system, such highly localized heat, transferred from the surface of GNRs to the surrounding environment, triggers a strong molecular motion of the guest molecules located within the micropores of the PCP shell and thereby results in their efficient release (Fig.1).

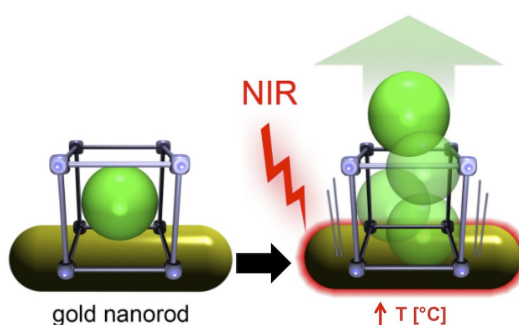


Fig.1 Conceptual scheme of the light-induced molecular release from a PCP/gold nanorod composite.

Thus, the key for the fabrication was to integrate PCPs and GNRs into core-shell structures, in which the PCP shell is grown in the vicinity of the surface of GNRs. Moreover, the thickness of the PCP shell had to be controlled in the mesoscale in order to effectively transfer the heat through the whole PCP crystal.

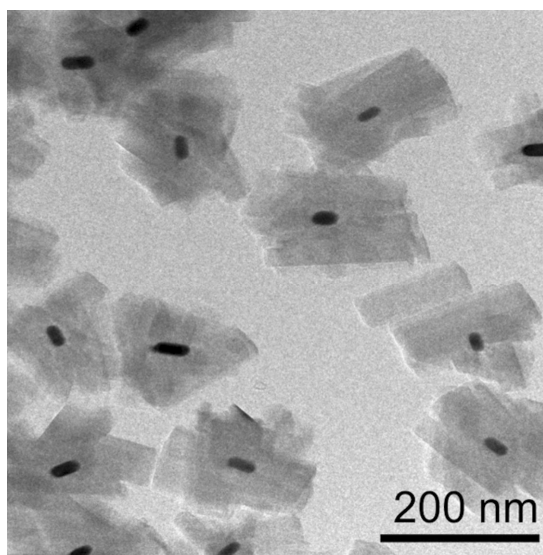
To reach a high enough degree of control upon PCP crystallization localization and PCP crystal size, we applied a unique method developed in our group, so-called "coordination-replication", which is based on a dissolution-recrystallization process. First, a thin layer of amorphous alumina was selectively deposited on the surface of individual gold nanorod. The alumina layer was then dissolved in the presence of a 1,4-naphthalene dicarboxylic acid ($H_2(1,4\text{-ndc})$) aqueous solution, under temperature and pressure condition for which the crystallization of the $[Al(OH)(1,4\text{-ndc})]_n$ PCP framework is favored.

Composites GNR@[Al(OH)(1,4-ndc)]_n particles in which individual gold nanorods were embedded within PCP crystal aggregates composed of few nanocrystals was hence generated.

4. 研究成果

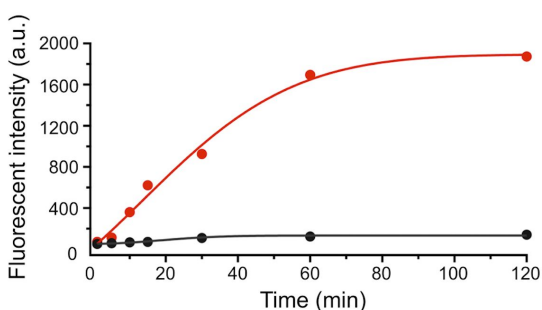
Well-defined $\text{GNR} @ [\text{Al}(\text{OH})(1,4\text{-ndc})]_n$ composite particles were synthesized by our strategy. Their core-shell nanostructure was evidenced by means of transmission electron microscopy (Fig.2) and energy-dispersive X-ray spectroscopy (EDX) mapping. Importantly, the transverse and longitudinal plasmon resonance bands of the GNRs were still observed by UV-vis spectroscopy after the composite formation, at 517 nm and 756 nm respectively. The microporosity of the PCP shell was also demonstrated by methanol adsorption measurements using quartz crystal microbalance (QCM) technique.

Fig.2 Transmission electron microscopy image of the composite $\text{GNR} @ [\text{Al}(\text{OH})(1,4\text{-ndc})]_n$ particles.



Light-triggered molecular release was confirmed using anthracene as fluorescent probe. While anthracene was strongly confined in the pores of $[\text{Al}(\text{OH})(1,4\text{-ndc})]_n$ due to the sufficient host-guest interaction, the heat production from the GNR core under NIR light irradiation induces the release of anthracene from the pores (Fig.3).

Fig.3 Evaluation of anthracene release from core-shell composites. The graphs show linear plots for fluorescence intensity maxima of the released anthracene versus time with (red) and without (black) NIR light irradiation.



At last, towards a spatial control of the molecular release, the $\text{GNR} @ [\text{Al}(\text{OH})(1,4\text{-ndc})]_n$ core-shell composites loaded with anthracene were also incorporated within polymer nanofibers via electrospinning. As polymer, we chose polymethylglutarimide (PMGI) nanofibers, which are biocompatible and easily patternable. In a near future, the incorporation of the core-shell composites within this organic one dimensional matrix is expected to allow for the control of their position as well as their integration into bioenvironments.

In conclusion, we have developed a strategy for controlling the molecular release from the pores of PCP crystals by combining the loading and unique guest stabilizing ability of PCPs with the photothermal properties of GNRs. In this system, GNRs are individually incorporated within the aggregates of PCP nanocrystals to form well-defined core-shell composites. The photothermal conversion ability of the GNRs acts as an optical switch that enables to remotely release the guest molecules adsorbed within the PCP pores through an increase of molecular mobility. Light-induced release of anthracene demonstrated the efficiency of this new molecular release system. We further demonstrated the method to incorporate the core-shell composites into biocompatible PMGI nano-fibers known to be good cell-culture scaffolds. This system will offer the possibility to spatially control the molecular release and to integrate them into biological systems for future applications in the field of cell biology. It can be anticipated that these PCP-based composites will be used as platform systems for the remote-controlled release of various relevant bioactive molecules to chemically stimulate living cells.

5. 主な発表論文等

(研究代表者、研究分担者及び連携研究者には下線)

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6 . 研究組織

(1) 研究代表者

Reboul Julien
京都大学・物質 細胞統合システム
拠点・助教
研究者番号 : 2 0 6 0 4 7 4 7