Journal of Physics and Chemistry of Solids 122 (2018) 218–226

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Preparation of calcium phosphate nanoparticles hybridized with europium (III) complex for novel luminescent organic-inorganic systems

Takuya Kataoka[a], Kenji Shinozaki[b], Shigeaki Abe[c], Motohiro Tagaya[a,*]

[a] Department of Materials Science and Technology, Nagaoka University of Technology, Kamitomioka 1603-1, Nagaoka, Niigata, 940-2188, Japan
[b] National Institute of Advanced Industrial Science and Technology (AIST), Midorigaoka 1-8-31, Ikeda, Osaka, 563-8577, Japan
[c] Graduate School of Dental Medicine, Hokkaido University, Sapporo, 060-8586, Japan

ARTICLE INFO

Keywords:
Organic-inorganic hybrid systems
Photofunctional interfaces
Calcium phosphate
Europium(III) complex
Luminescent nanomaterials

ABSTRACT

We have synthesized novel inorganic–organic hybrid systems based on the interactions between calcium phosphate (CP) and tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium (III) (EuTH) complex to clarify the states of the EuTH molecules. We achieved the nucleation and crystal growth of electronically localized of EuTH molecules using two different synthetic processes (based on the timing of the addition EuTH before and after the CP nucleation stage). The coordination environment of the Eu^{3+} ion inside/on the hybrids was clearly changed, having the higher spatial symmetry states in the hybrid. The aspect ratios of the hybrid crystallites were 2.5–6.0, suggesting that the EuTH molecules selectively interacted with the *a*–plane of the CP nuclei to induce preferential crystal growth along with the uncovered *c*–plane. The segregated EuTH molecules on CP surfaces suppressed Ca^{2+} dissolution from the hybrids in phosphate buffer saline. In the excitation spectra of the hybrids, the ${}^7F_0 \rightarrow {}^5L_6$ transition appeared as a result of the interaction between the EuTH and phosphate ions, suggesting that the phosphate ions affected the coordination environment. In the luminescence spectra of the hybrids, the luminescence intensity ratio of the magnetic dipole transition (${}^5D_0 \rightarrow {}^7F_1$) to electric dipole transition (${}^5D_0 \rightarrow {}^7F_2$) were higher than those of EuTH and the other Eu^{3+}-doped inorganic systems. Thus, the higher spatial symmetry states of the Eu^{3+} ion in the hybrids resulted in greater luminescence intensities and quantum efficiencies, which would be affected by the phosphorus anti-quenching. In the future, CP hybrids with various organic complexes will be prepared, and these could be applied in the biomedical fields such as in bio-imaging and drug delivery systems.

1. Introduction

An important biomaterial, hydroxyapatite (HAp: $Ca_{10}(PO_4)_6(OH)_2$), which is a type of calcium phosphate (CP), has excellent properties such as high biocompatibility, biological activity, and biodegradability [1–5]. HAp is the main component of bone *in vivo*. The structural calcium (II) ions (Ca^{2+}) form the chemical bonds with the oxygen atoms of collagen molecules at the interface, resulting the inorganic/organic hybrid functions of bone tissue. Thus, the Ca^{2+} ions can play an important role in biomineralization processes [6,7]. To understand how to control the HAp functions *in vivo* and *in vitro*, the investigation of the hybrid originating from the interactions between HAp and organic molecules is important. Although researchers have intensively investigated the hybrids of the HAp with polymers such as collagen, chitosan, and polylactic acid, which mimic the bone functions [8–14], the hybrid interface state has not been identified.

The HAp crystals hybridized with functional small molecular compounds such as 8-hydroxyquinoline (8Hq), chondroitin sulfate, and glucosamine at the nanoscales have been reported [15–18]. In the HAp/8Hq system, the photofunctions of the hybrids have been successfully demonstrated to result from the interfacial chemical bonds [15,16]. We have synthesized europium (III) ion (Eu^{3+})-doped HAp in the presence of cetyltrimethylammonium bromide (CTA^+Br^-) micelles to elucidate the importance of the interfacial interactions between $CTA^+ - PO_4{}^{3-} - Eu^{3+}$ for the photofunctions [19,20]. As another hybrid system, the hybrid particles of the HAp with porphyrin molecules have been reported [21,22]. Therefore, an understanding of the physicochemical driving force for the interfacial complexation of organic molecules at the HAp surfaces is essential for designing of novel optoelectronic biomaterials.

As functional small molecular compounds, trivalent lanthanide complexes with organic ligands are interesting because of their luminescent properties. Lanthanide complexes possess of the characteristic and narrow luminescence spectral lines and long-lived excited states

---

[*] Corresponding author. Tel.: +81 258 47 9345.
E-mail address: tagaya@mst.nagaokaut.ac.jp (M. Tagaya).

https://doi.org/10.1016/j.jpcs.2018.06.031
Received 28 March 2018; Received in revised form 4 June 2018; Accepted 23 June 2018

because of the luminescent centers of trivalent lanthanide ions [23]. The organic ligands can effectively increase the light absorption [24], and the spectral shapes depend on the electronic environment, although the Ln^{3+} ions alone have poor light absorption abilities because of the forbidden intraconfiguration *f-f* transition [25]. Lanthanide complexes have been incorporated into inorganic porous matrixes such as zeolites [26,27] and mesoporous silicas [28,29] to form organic-inorganic hybrids. The confinement of the lanthanide complexes within the inorganic porous structures not only improves their stabilities but also decreases the aggregation-induced quenching among the lanthanide complexes, which would be useful for achieving effective luminescence [30]. However, the hybrids with the biocompatible materials such as CP and their luminescent properties based on the inorganic/organic interfaces have not been reported so far.

In this study, novel inorganic/organic nanohybrids of CP and the tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium (III) (EuTH) complex, denoted the ECP hybrid, were prepared, and their physicochemical properties were investigated. We propose here that nucleation and subsequent crystal growth can occur from the EuTH complex because charge-transfer [31] from the central Eu^{3+} ion to the organic ligands occurs in the molecules, and the electrically charged molecules interact with the Ca^{2+} and phosphate ions. Thus, the Eu^{3+} ion complexed with organic ligands can act as the nucleation site to form novel luminescent hybrids. In this work, the time of addition of the EuTH complex was controlled; that is, the complex was added either before and after nucleation, as shown in Scheme 1. This resulted in the EuTH being captured the inside CP or the complexes being segregated on CP, denoted the ECP1 and ECP2 hybrids, respectively.

2. Experimental

2.1. Materials and preparation

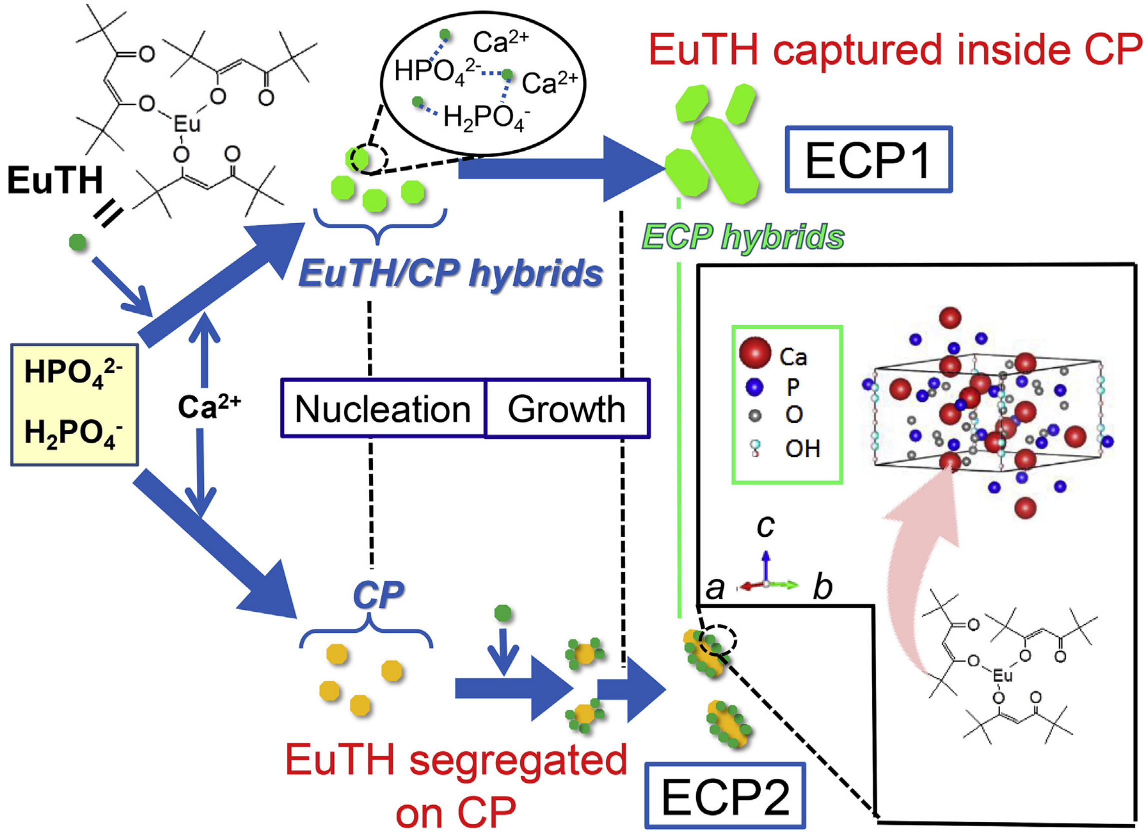
Two different ECP hybrids were prepared by adding EuTH at different stages of the synthesis, as shown in Scheme 1. All the reagents were purchased from Wako Chemical Co., Ltd. and used without further purification.

For the synthesis of the ECP1 hybrid, 0.1 mmol of EuTH was dissolved in 20 ml of ethanol and ultrasonically treated for 10 min to form EuTH/ethanol. Then, 50 ml of ultrapure water containing 6 mmol of K_2HPO_4 was dropped into the EuTH/ethanol, and the pH was adjusted to 12 using tetramethylammonium hydroxide (TMAOH). Next, 30 ml of ultrapure water containing 9.9 mmol of $CaCl_2{\cdot}2H_2O$ was added to the EuTH/ethanol/K_2HPO_4 aqueous solution at a rate of 1 ml/min to obtain the ECP1 precursor. Here, the initial Eu concentration of Eu to (Ca + Eu) was 1.0 mol%, and the molar ratio of (Ca + Eu) to P was 1.67.

In addition, the order of the addition of calcium and phosphate sources was reversed, but the amounts of regents are same as the ECP1 procedure. The ultrapure water containing $CaCl_2{\cdot}2H_2O$ was dropped into the EuTH/ethanol. Then, ultrapure water containing K_2HPO_4 was added to the EuTH/ethanol/$CaCl_2$·aqueous solution to obtain the "EuTH/Ca–P" precursor.

In the ECP2 hybrid synthesis, the amounts of reagents are the same as the procedure of ECP1. K_2HPO_4 was dissolved in ultrapure water and the pH was adjusted to be 12 using TMAOH. The ultrapure water containing $CaCl_2{\cdot}2H_2O$ was added to the K_2HPO_4 solution. Then, the solution was added to the EuTH/ethanol solution to obtain the ECP2 precursor.

The precursors prepared above were refluxed at 40 or 80 °C for 3 h, but and the EuTH/Ca–P precursor was refluxed at 80 °C. The precipitation products were washed once with ethanol and ultrapure water



Scheme 1. Novel synthetic two processes for the ECP hybrids to produce ECP1 and ECP2.