Polymer-Based Near-Infrared Afterglow Fluorescent Complex of Dye and Rare-Earth-Doped Ceramics

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Near-infrared (NIR) light has been used for in vivo deep imaging in the biomedical field owing to its high permeability in biological tissues. Conventional fluorescence bioimaging requires simultaneous optical excitation, which can induce undesired results such as autofluorescence. In the present study, we report a polymer-based NIR afterglow fluorescent complex by using NIR dye, LDS 821, and SrAl₂O₄: Eu, Dy powder. To obtain the complex, SrAl₂O₄: Eu, Dy was first mixed with LDS 821 solution and dried at 65 °C for 12 h. Then, they were further mixed with pentaerythritol tetraacrylate (PETA) and photopolymerization initiator and then subjected to phopolymerization reaction. Poly-PETA was effective for not only retain both the dye and inorganic powder but also preventing the denaturation of SrAl₂O₄: Eu, Dy by water. The obtained polymer-based complex emits NIR afterglow fluorescence (wavelength: 760−780 nm) with a long fluorescence lifetime (5.0 min). This material design will provide a choice of obtaining NIR luminescent imaging phosphors for deep tissues without simultaneous light irradiation during image acquisition.

Keywords: Afterglow fluorescence, Near-infrared, Rare-earth-doped ceramics, Polymer

1. Introduction

Fluorescent bioimaging has been a major technique to dynamically visualize biological phenomena and tissue structures by using fluorescence probes. The light in near-infrared (NIR) wavelength region (700−2400 nm) shows less optical loss and scattering by biological tissues than those of visible and ultraviolet regions. Thus, the NIR window has been used for in vivo deep imaging [1, 2]. While indocyanine green has been used as the most major NIR fluorescent probe in clinical field, various types of NIR phosphors that work in longer wavelength (>1000 nm) have been developed [3] such as single-walled carbon nanotubes [4–8], quantum dots [9,10], rare-earth-doped ceramics [11–15], and organic dyes [16–20]. Although they are useful for in vivo fluorescent imaging of deep tissues, conventional fluorescence bioimaging with these phosphors requires simultaneous optical excitation, which can also induce autofluorescence and decrease the signal-to-noise ratio. To solve this problem, an NIR optical imaging method free from simultaneous light irradiation during image acquisition has been studied.

Afterglow fluorescence is a phenomenon in which a luminescent material continues to emit light for several seconds to hours after the irradiation for excitation is removed. This is useful for realizing the imaging free from simultaneous irradiation for excitation. The most representative and commercially available afterglow phosphor is rare-earth-doped ceramics, SrAl₂O₄: Eu, Dy marketed as Luminova, which emits visible light with a peak wavelength of 540 nm. In this phosphor, Dy and Eu work as a trap center and emitting center, respectively [21]. Recently, zinc gallogermanate co-doped with Cr³⁺/Pr³⁺ [22] and LaAlO₃ perovskite co-doped with Cr³⁺/Er³⁺ [23] were reported as NIR afterglow phosphors emitting 700 and 1550 nm, respectively. Red shifting of the afterglow fluorescence of SrAl₂O₄: Eu, Dy has also been reported. Coating the surface of SrAl₂O₄: Eu, Dy with poly(methyl methacrylate) and red-emitting
coumarin converted the wavelength peak of the afterglow fluorescence from 525 nm (green) to 610 nm [24]. However, the color conversion of the afterglow fluorescence of SrAl2O4: Eu, Dy from green to NIR has not been reported. Moreover, the potential of denaturation of SrAl2O4: Eu, Dy by water should be investigated to prevent its quenching in the physiological environment.

In the present study, we chose an organic dye, LDS 821, as a color converter from green to NIR. To design a material that emits NIR afterglow luminescence, fixing of the LDS 821 at the surface of SrAl2O4: Eu, Dy with poly-PETA, a hydrophobic polymer that can shield rare-earth-doped ceramics from surrounding aqueous environment [25]. The spectra and the decay rate of the afterglow fluorescence were investigated for the obtained polymer-based complex with LDS 821 and SrAl2O4: Eu, Dy.

2. Experimental

2.1. Materials

A ceramic-based green afterglow fluorophore SrAl2O4: Eu, Dy (Luminova; G-300L700) was purchased from Nemoto & Co., Ltd. (Kanagawa, Japan). LDS 821 (excitation: 532 nm, emission: 825 nm) and Irgacure 784 were purchased from Lambda Physik Inc. (FL, USA) and Ciba Specialty Chemicals Inc. (Basel, Switzerland), respectively. Pentaerythritol tetraacrylate (PETA) and dimethyl sulfoxide (DMSO) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). LDS 821 was used as a solution in DMSO at the concentration of 100 mg/mL. All the reagents were used without further purification.

2.2. Preparation of polymer-based complex of rare-earth-doped ceramics and dye

SrAl2O4: Eu, Dy (0.15 g) and LDS 821 (100 μL) were mixed and dried by incubating at 65 °C for 12 h. After cooling to room temperature, the dried mixture was mixed with PETA (0.14 g) and Irgacure 784 (2 mg) and then placed on a 1-mm-thick glass slide (Matsunami Glass Ind., Ltd., Osaka, Japan). The sample was irradiated by a light of halogen lamp (25 W/cm², LA-150UE; Hayashi-Repic Co., Ltd., Tokyo, Japan) for 12 h to photopolymerize the PETA.

2.3. Optical characterization of the polymer-based complex

The afterglow fluorescent spectra of samples were analyzed by using a spectrometer (Flame-S; Ocean Optics Inc., Tokyo, Japan) at 0–20 min after switching off the 2-min irradiation of light from a halogen lamp (25 W/cm²; LA-150UE).

3. Results and discussion

3.1. Polymerization of PETA with dye and rare-earth-doped ceramics

First, we tried to prepare polymer-based complex of LDS 821 and SrAl2O4: Eu, Dy by mixing them with PETA and the photopolymerization initiator, Irgacure 784, without the process for drying the dye-ceramics mixture followed by lamp irradiation. In this case, the blue color of LDS 821 was severely lost by the photopolymerization process (Fig. 1). This result was also observed when 2,2'-azodiisobutyronitrile was used for photopolymerization initiator (data not shown).

![Fig. 1. A false example of preparation of the polymer-based complex. The LDS 821 dye was severely denatured (thus its dark blue color was lost) via radical generation from Irgacure 784 by irradiation for photopolymerization.](image)

This denaturation of LDS 821 was suppressed by immersing SrAl2O4: Eu, Dy in LDS 821 solution in DMSO at 65 °C for 12 h before adding PETA and Irgacure 784. The results suggest that LDS 821 was denatured by radicals generated from Irgacure 784 during the light irradiation in the first case. Therefore, we mixed SrAl2O4: Eu, Dy with LDS 821 and dried before the photopolymerization to obtain polymer-based complex for following experiments (Fig. 2a).

3.2. Effect of poly-PETA coating on the luminescence of rare-earth-doped ceramics in water

The quenching of SrAl2O4: Eu, Dy has been reported following denaturation in water [26]. The quenching is likely due to the hydroxylation of SrAl2O4 [26]. To investigate the effect of poly-PETA coating on the luminescence, we first prepared a polymer-based complex without the NIR dye, LDS 821. The afterglow fluorescence intensity of pure SrAl2O4: Eu, Dy decreased to 12.5% by exposure to water for 24 h, while the intensity of poly-PETA-coated SrAl2O4: Eu, Dy maintained at 87.2% after the incubation in water (Fig. 2b). The results showed that poly-PETA successfully coated...
SrAl₂O₄: Eu, Dy via photopolymerization and prevented its denaturation and quenching by water. The shift of luminescence spectral peak was observed by sample coating with poly-PETA possibly due to the effect of optical absorption of Irgacure 784 used as a photopolymerization initiator.

3.3. Near-infrared afterglow fluorescence of the dye-ceramics complex in poly-PETA

Finally, we investigated the NIR afterglow fluorescence of the polymer-based complex. As shown in Fig. 2c, it emits NIR light from LDS 821 excited by afterglow fluorescence of SrAl₂O₄: Eu, Dy in the complex for several tens of minutes after switching off the irradiation for excitation of SrAl₂O₄: Eu, Dy. The fluorescence lifetime determined by the decay curve (Fig. 2d) was 5.0 min, which is similar to visible afterglow fluorescence of SrAl₂O₄: Eu, Dy [21]. Although further investigations are needed to enhance the afterglow fluorescence of NIR and to increase its biocompatibility to allow various applications, the concept presented in this paper will provide a new choice of obtaining NIR luminescent imaging phosphors for deep tissues without simultaneous light irradiation during image acquisition.

4. Conclusion

In the present study, we developed a polymer-based NIR afterglow luminescent complex using rare-earth-doped ceramics, SrAl₂O₄: Eu, Dy, and an NIR dye, LDS 821. The coating of poly-PETA resulted in protecting the SrAl₂O₄: Eu, Dy from quenching by water. By excitation with afterglow luminescence (wavelength: 540 nm) of SrAl₂O₄: Eu, Dy, the complex obtained shows NIR fluorescence (wavelength: 760–780 nm) with slow decay rate (lifetime: 5.0 min) that is similar to the afterglow luminescence of the original SrAl₂O₄: Eu, Dy. This concept of designing afterglow NIR phosphor may develop new NIR luminescence bioimaging techniques for deep tissues without simultaneous irradiation for excitation during image acquisition.

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