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Photothermally induced release from liposome suspended in mixture solution of gold nanoparticle and thermo-sensitive polymer

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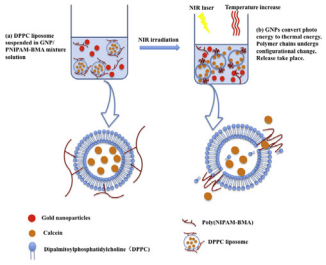
HIGHLIGHTS

- Gold nanoparticles (GNP)/PNIPAM-BMA mixture are mixed with DPPC liposome.
- The temperature of suspension increases due to the treatment of near infrared (NIR) irradiation to GNP.
- A stepwise release takes place under NIR irradiation for the thermal contraction of the thermo-sensitive copolymer and the phase transition of the liposome membrane.

GRAPHICAL ABSTRACT



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ABSTRACT

The release profiles of calcein from dipalmitoylphosphatidylcholine (DPPC) liposome, with/without gold nanoparticle (GNP) and poly(N-isopropylacrylamide-co-butylmethacrylate) (PNIPAM-BMA), were observed as function of temperature and NIR irradiation. DPPC liposome without GNP/copolymer released calcein substantially only when the temperature was higher than the phase transition temperature (PTT, 41 °C) of the liposome membrane. Meanwhile, the liposome with GNP and PNIAPM-BMA released its payload even below PPT (e.g. even at 37 °C). The thermal contraction of the thermo-responsive polymer would be responsible for the release occurred below PPT. On the other hand, under NIR irradiation, DPPC liposome with GNP and PNIPAM-BMA showed a stepwise release. The first step of release is possibly due to the thermal contraction of the polymer and the second step of release is possibly because of the phase transition of the liposome membrane. The photothermal energy generated by GNP could be responsible for the NIR irradiation-triggered release.

1. Introduction

Temperature-sensitive liposome can be prepared by taking advantage of either the phase transition of the phospholipid bilayer of liposomal membrane or the phase transition of thermo-responsive polymers immobilized on the membrane. The phospholipid bilayer undergoes the solid gel-to-liquid crystal transition at a specific temperature and the phase transition temperature (PTT) is proportional to the length of the acyl chain of phospholipid [1–5]. For the preparation of temperature-sensitive liposome, dimirystoyl phosphatidylcholine (DMPC), dipalmitoyl phophatidylcholine (DPPC), and distearoyl phosphatidylcholine (DSPC) are usually used as a phospholipid, and the PTT of their liposomal membrane is 24 °C, 42 °C, and 55 °C, respectively [6–9]. The permeability of water-soluble compounds through the liposomal membrane markedly increases at PTT, giving a rise to temperature-sensitive release [9,10]. On the other hand, thermo-responsive polymers exhibiting lower critical solution temperature (LCST)

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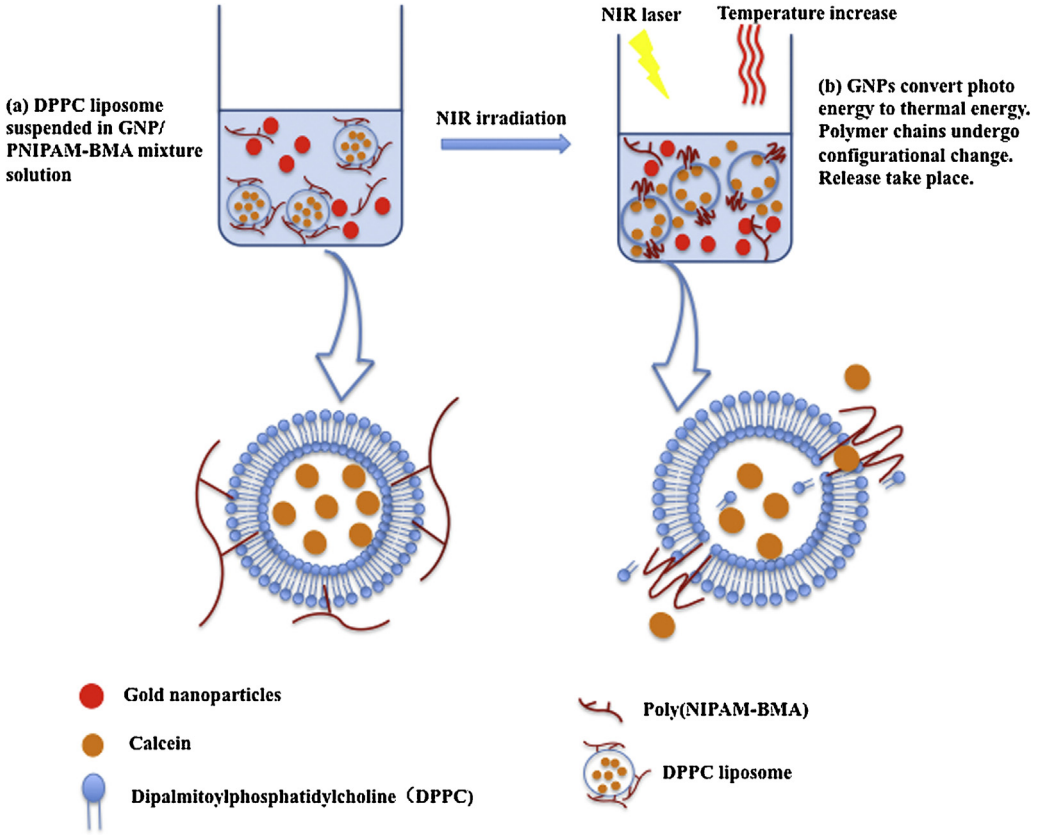

Fig. 1. DPPC liposome suspended in GNP/PNIAPM-BMA mixture solution. Under NIR-irradiation, GNP can convert photo energy to thermal energy due to its SPR and the thermal energy will increase the temperature of the liposomal suspension. As a result, the thermo-sensitive polymer chains can undergo configurational change from an expanded form to a contracted form and the liposomal membrane will be subjected to solid gel-to-liquid crystal transition, leading to a stepwise release.

cause liposomes to release their content in a temperature-sensitive manner when the polymers are immobilized on the liposomal membrane. Poly(*N*-isopropylacrylamide) and Pluronic F127 are frequently used as a thermo-responsive polymer [11–13]. Below LCST, the polymer chains take an expanded form in an aqueous phase. When the solution temperature increases across LCST, the chains collapse to be a condensed form [11–14].

It was reported that the thermal contraction of the polymer chains imposes a mechanical stress on the liposomal membrane, giving a rise to temperature-sensitive release [14–18]. Recently, photo-sensitive liposome has been developed by incorporating gold nanoparticles (GNP) in temperature-sensitive DMPC/DPPC liposome [19,20]. Under the irradiation of NIR, GNP generates heat owing to the surface plasmon resonance (SPR) and the liposome releases its payload in response to the temperature change. Recently, liposome decorated with gold nanoparticles was reported to release its content in response to temperature change and light irradiation [21].

In this study, DPPC liposome was mixed with GNP and poly(N-isopropylacrylamide-co-butylmethacrylate) (PNIPAM-BMA, a thermo-sensitive polymer exhibiting LCST), and the effect of temperature and NIR irradiation on the release degree of calcein (a water-soluble fluorescent dye) from the liposome was investigated. Under NIR irradiation, GNP can convert photo energy to thermal energy due to its photothermal conversion property and the thermal energy will increase the temperature of the liposomal suspension. As a result, the thermo-sensitive polymer chains can undergo configurational change from an expanded form to a contracted form and the liposomal membrane will be subjected to solid gel-to-liquid crystal transition. Accordingly, DPPC liposome suspended in GNP/PNIPAM-BMA mixture solution can show a stepwise release, because not only the thermal contraction of the thermo-responsive polymer but also the phase transition of the liposome membrane can act as a trigger for the release (Fig. 1). Since DPPC liposome coexists with not only GNP but also a thermo-responsive polymer, the liposome can exhibit the first step of release, caused by the thermal contraction of the thermo-responsive polymer, and the second step of release, induced by the phase transition of the liposome membrane. The photothermal triggerable liposome studied in the present work could be applied to the development of drug carriers which release their content in a controlled manner in answer to NIR irradiation.

2. Materials and methods

2.1. Materials

1,2-Dipalmitoyl-sn-glycero-3-phosphocholine (DPPC), Butyl methacrylate (BMA), Sodium citrate dehydrate, calcein and 1,4-dioxane were purchased from Sigma–Aldrich Co. (St. Louis, MO, USA). Hydrogen tetrachloroaurate (III) tetrahydrate was purchased from Wako (Osaka, Japan). a-a′-Azobis(isobutyronitrile) (AIBN) was provided by Junsei Chemical Co. (Japan). *N*-isopropylacrylamide was purchased from Tokyo Chemical Co. (Japan). N-(2-hydroxyethyl) piperazine-n′-(2-ethanesulfonic acid) (HEPES) was obtained from USB corporation (Cleveland, OH, USA). Sephadex G 100 was provided by GE Healthcare (Sweden). Water was doubly distilled in a Milli-Q water purification system (Millipore Corp, MA, USA) until the resistivity was 18 MΩ/cm. All other reagents were in analytical grade.