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Precise stimulation of near-infrared light responsive shape-memory polymer composites using upconversion particles with photothermal capability

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ABSTRACT

The incorporation of thermally-induced shape-memory polymer (SMP) with photothermal fillers has been widely used in creating photoresponsive SMP composites (SMPCs). Near-infrared (NIR) light, which is safer for human tissues and naked eyes, has been widely used to trigger such intelligent SMPCs containing carbon nanomaterials, metal nanoparticles, or rare earth organic complexes. There is still a need to aim invisible NIR light beam remotely onto SMPCs to realize the precise shape recovery of their featured areas. Here, $NaYF_4$:99.5%Yb^{3+}, 0.5%Tm^{3+} particles presenting both upconversion and photothermal capabilities were utilized as multifunctional fillers in a crosslinked copolymer of methyl methacrylate and butyl acrylate, enabling the prepared SMPCs to transfer the NIR light at 980 nm simultaneously into both visible light and heat. The particles with a low content up to 1 phr did not vary the crosslinking level and glass transition temperature of the SMPC. With the aid of upconversion at a relatively low power density, the position of laser beam on SMPC surface was detected easily, facilitating the aim towards the area anticipated to be triggered without inducing a shape deformation. The subsequent increase in power density successfully resulted in the precise shape recovery with the recovery ratio higher than 90%. The concept of precise location before stimulation was demonstrated in the cases of multiple shape deformations, remote activation in the darkness, and microscale structured surfaces. The reported multifunctional nanoparticles truly executed the remote and precise trigger of SMPCs using invisible NIR light, which can be further exploited in other thermally-induced smart polymer composites.

1. Introduction

Shape-memory polymer (SMP) as an extensively reported intelligent polymer can be programmed into a temporary shape and upon specific stimulus recall its original shape [1–3]. So far, thermally-induced SMPs have been widely investigated, allowing shape recovery when the bulk temperature via direct heating reaches their switching temperatures (T_{sw}s) [1–3]. The requirement to drive polymer movements in an indirect manner explores the development of SMPs triggered by magnetic field [4,5], electric field [6–8], or light [9–20]. By contrast, photo-induced SMPs attract increasing attentions and have been used in actuators [21,22], biomedical devices [22–24], self-oscillation devices [25], and so on, because light allows for the combination of remote activation, spatial control, precise localization, and instantaneous on-off.

One simple approach to create photoresponsive SMP is to mix thermally-induced SMPs with photothermal fillers, including organic dyes [12,13], carbon nanomaterials [14,15], metal nanoparticles [16–19], and rare earth organic complexes [20], to prepare SMP composites (SMPCs). The recall of permanent shapes occurs

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when the indirectly generated temperature resulting from functional fillers approaches T_{sw}. However, the reported photothermal fillers merely act as one role in transferring remote light energy into single energy form of heat. In comparison to UV and visible light, near-infrared (NIR) light beam is relatively safer for human bodies and naked eyes. However, the obvious disadvantage of NIR light, which cannot be overlooked, is its invisibility, i.e., it is unable to detect the position of a laser beam on SMPC specimens. As a result, NIR light cannot be competent with visible light whenever a precise and remote trigger of complex deformation is required. Therefore, for the purpose of expanding the utilization of NIR light in photo-responsive SMPCs, it is an urgent need to clearly see the position of NIR light on SMPCs before featured areas are precisely triggered.

Hexagonal $NaYF_4$ crystals are well known for its upconversion capability of absorbing NIR photons, such as 980 nm, to emit visible and ultraviolet photons [26–31]. Yb^{3+} ions are usually co-doped as sensitizer with large absorption cross section of $^2F_{7/2}$ to $^2F_{5/2}$ transition to Tm^{3+} lanthanide activators to enhance the 980 nm to visible upconversion emission [27,28]. Therefore, $NaYF_4$:Yb^{3+}, Tm^{3+} nanoparticles offers a potential candidate in detection and localization of laser beam on NIR light responsive SMPCs. Nevertheless, we are concerned about the possibility that the combination of upconversion fillers with conventional photothermal fillers would lead to potential interference. For instance, the dark color coming from carbon nanomaterials could impair the upconversion luminescence. Herein, it brings up a question that whether such upconversion nanoparticles themselves can play an additional photothermal role resulting from the energy dissipation as heat in self-luminous behavior to trigger the shape recovery of SMPCs. If so, with the unique capability of transferring NIR light of 980 nm simultaneously into two energy manners of visible light and heat, $NaYF_4$:Yb^{3+}, Tm^{3+} nanoparticles can be utilized as multifunctional fillers in NIR light-induced SMPCs, to realize a new concept that via self-luminous behavior, the detection of NIR laser beam on specimens facilitates the aim towards certain areas before shape recovery is subsequently stimulated in a precise fashion.

In the present work, $NaYF_4$:x% Yb^{3+}, 0.5% Tm^{3+} particles with different contents of doped Yb^{3+} ions (x = 10, 15, 20, 40, 60, 80 and 99.5) were first prepared. Their upconversion and photothermal capabilities upon the irradiation of NIR light at 980 nm were evaluated, while the selected powder presenting the best upconversion and photothermal functions was subsequently dispersed in a thermally-induced SMP, consisting of methyl methacrylate and butyl acrylate. The particle effects on crosslinking density and glass transition temperature as T_{sw} were studied. Subsequently, in addition to shape recovery ratio, upconversion and photothermal capabilities of the SMPCs containing different particle loading upon the irradiation of NIR light at 980 nm were investigated as well. Finally, the feasibility of such SMPCs to achieve the multiple shape deformations, remote activation in the darkness, and the precise stimulation of microscale structures was demonstrated.

2. Experimental section

2.1. Materials

$YCl_3 \cdot 6H_2O$ (99.99%), $YbCl_3 \cdot 6H_2O$ (99.99%), and $TmCl_3 \cdot 6H_2O$ (99.99%) were purchased from Beijing Founde Star Science & Technology Co., Ltd. Oleic acid (OA), 1-octadecene (ODE), *n*-butyl acrylate (BA), methyl methacrylate (MMA), ethylene glycol dimethylacrylate (EGDMA), and 2,2′-azobis(2-methylpropionitrile) (AIBN) were all obtained from Alladin, China. NaOH, NH_4F, cyclohexane, ethanol, methanol, tetrahydrofuran (THF) and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. Polyethylene glycol (PEG)-monooleate was achieved from Sigma Aldrich. All the chemicals were used without further purification.

2.2. Synthesis of $NaYF_4$:Yb, Tm particles

The multifunctional particles were prepared using a thermal decomposition method according to a previous research [30]. Typically, 3 mmol $LnCl_3 \cdot 6H_2O$ (Ln = Y, Yb, Tm) with 30 mL of OA and 30 mL of ODE were added into a 100 mL three-necked flask with high-purity N_2 flow. The mixture was heated at 160 °C with strong stirring for 45 min. The solution was then cooled down to 60 °C, before 20 mL of methanol solution containing NH_4F (12 mmol) and NaOH (7.5 mmol) was added dropwise with a flow of N_2. Another 20 min was allowed for formation of crystal nuclei. Subsequently, the reaction vessel was heated to 100 °C and maintained for 10 min for methanol evaporation, and heated to 310 °C to ensure particle growth within 60 min under the flow of N_2. After cooling the solution down to room temperature naturally, the particles were generated by precipitation using 20 mL ethanol and stirring for 5 min. The particles were finally collected using centrifugation and washed three times with ethanol.

2.3. Preparation of P(MMA-co-BA) with well-dispersed particles

MMA and BA monomers with the molar ratio of 7:3, EGDMA (5 phr) and AIBN (0.6 phr) were added into the DMF (4 g) subsequently. At 65 °C, the whole mixture was prepolymerized in a glass vial (20 mL) for 30 min and was injected into a home-made glass container ($L \times W \times D = 70$ mm $\times$ 20 mm $\times$ 1 mm), allowing further copolymerization in an oven at 65 °C for 12 h. The materials were then removed and then treated at 65 °C for 24 h in a vacuum oven. Three different particle loadings (0.2, 0.5 and 1 phr) were used in the copolymer with the MMA:BA molar ratio of 7:3. The particles were first dispersed in THF (0.5 g) with the desired amount of PEG-monooleate and sonicated for 30 min. The weight ratio of particles and PEG-monooleate was 1:4. After evaporation of THF, the chemicals were added into the same glass vial, initiating the subsequent polymerization as described above.

2.4. Characterizations

The luminescence spectra were recorded using a fluorescence spectrophotometer (Jobin Yvon FL3-221, Horiba, Japan) equipped with a 980 nm laser (KS3-11312-912, BWT Co., China) as the excitation source. The dispersion of nanoparticles (0.2, 0.5, and 1 phr) in P(MMA-co-BA) was examined using an optical microscopy (BA210, Motic China Group Co., Ltd.). The 980 nm NIR light was given generated by a laser diode driver (KS3-11312-912, BWT Co., China). The temperatures of the particles and copolymers were measured using an infrared camera (A600-Series, FLIR, USA) which was operated through commercial software (BM_IR, Version 7.2), while the thermal-infrared images were captured as well. The temperature was recorded after the irradiation for 3 min when thermal equilibrium has been reached. A rheometer (MCR302, AntonPaar, Austria) which has a function of dynamical mechanical analysis (DMA) in a torsion mode was used to measure the glass transition temperature. The temperature scanning range was from -75 to 200 °C at a heating rate of 3 °C min^{-1}, while the frequency was 1 Hz.

A piece of the copolymer with the mass of m_1 was cut and immersed in DMF. After 72 h, the sample was removed from solvent, while the mass (m_2) was immediately measured in swollen state after cleaning the extra solvent with tissue. The swollen sample was heated at 60 °C until complete dry to obtain the final weight (m_3). The gel content was (G) given by $m_3/m_1 \times 100\%$. And the swelling ratio (Q) was calculated using Equation (1). The ρ_1 and