



# Shape-memory polymer composites selectively triggered by near-infrared light of two certain wavelengths and their applications at macro-/microscale

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## ABSTRACT

A cost-efficient filler system based on rare earth organic complexes of Yb(TTA)<sub>3</sub>Phen and Nd(TTA)<sub>3</sub>Phen is reported, showing selective photothermal effect to near infrared (NIR) light of 980 and 808 nm, respectively. The integration of the two fillers into a commercially available SMP of poly[ethylene-*ran*-(vinyl acetate)] (EVA) respectively provide selective NIR light responsive SMP composites (SMPCs), while their full shape recoveries triggered by NIR light of 980 or 808 nm are correspondingly realized. In addition, the NIR light irradiation periodicity is varied and the results suggests that reducing deformation temperature ( $T_{\text{deform}}$ ) of EVA caused the shape recovery at a relatively short exposure time, while long irradiation time must be allowed to trigger the shape deformation at a high  $T_{\text{deform}}$ . A macroscaled actuator with multi-shaped variation is demonstrated via sequential irradiations of NIR lights of 980 and 808 nm. More interestingly, the shape recovery of a certain pattern on the micropatterned surface consisted of the two composites is triggered first upon one NIR irradiation before the remaining patterned area is stimulated using another NIR wavelength. This work integrates more capabilities into light-induced SMPCs, including multi-shape deformation both at macro and microscale, as well as unique responsive signal, in addition to the known remote and noncontact control.

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## 1. Introduction

Shape-memory polymers (SMPs) have found applications in many fields, including biomedical devices, self-deployable instruments, actuators, and smart textiles, to name a few [1–4]. The trends towards investigating SMP structures at micro/nanoscale and miniaturization of SMP devices are also of increasing interest because of the usage in switching adhesion or optical property as well as directing cell growth [5–9]. Upon stimulus, usually heat,

SMPs recall their original shape from programmed temporary one when the temperature goes beyond their switching temperature ( $T_{\text{sw}}$ ) [4]. In comparison with heat, light enables the “on-demand” triggering of SMPs in a remote, localized and non-contact manner with neglected intervention on surrounding circumstance [10,11]. To date, introduction of photothermal fillers into thermally-induced SMPs have been widely reported as one convenient and commercially available approach to prepare such light-induced SMP composites (SMPCs) [12–23]. Under irradiation, the fillers absorb the light energy and transfer it into heat, indirectly increasing the temperature of the composites. Shape recovery occurs when the temperature reaches the  $T_{\text{sw}}$ .

Functional photothermal fillers responsive to different light wavelengths, including UV light, visible light, and infrared light, have been explored to fabricate light-induced SMPCs. A metallosupramolecular unit formed via coordinating Mebip ligands to Zn(NTf<sub>2</sub>)<sub>2</sub> was introduced into an epoxy resin to turn UV light into

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heat [14]. In addition, a visible light beam of 532 nm was irradiated onto crosslinked polyethylene oxide with a very small amount of Au nanopowders [15]. The surface plasmon resonance of Au nanopowders resulted in the temperature increase and correspondingly the shape deformation. Light responsive SMPC micropillars in a hexagonal array were prepared based on epoxy/Au nanorods, while the visible light laser of 532 nm was also utilized as the light source [17]. One main advantage of visible light is the easy location of beam on the samples to achieve complex shape deformation [16]. In comparison with UV and visible light, near-infrared (NIR) light is not absorbed greatly by biological systems and thus considered as a safe actuation source to trigger the shape deformation of SMPCs [24]. Via selective deposition of black ink onto hinge area, irradiation of NIR light of 988 nm as a widely reported NIR light source resulted in the self-folding of polymer sheets [19]. And the NIR light of 808 nm was utilized to trigger the shape recovery of a polycaprolactone (PCL) based SMPCs mixed with multi-walled carbon nanotubes (CNTs) and reduced graphene oxides [23]. Besides, gold nanorods were introduced into crosslinked PCL and used the NIR light of 805 nm to stimulate the shape change of surface nanopatterns to direct cell growth [9].

SMPs with multiple shape variation have attracted significant attention [25,26]. The development of photothermal filler selectively responsive to a certain light wavelength has attracted interest to facilitate the complex or successive multi-shape change of polymers, exploring the applications in microfluidic devices or smart actuators. To date, however, only a few selective filler systems were successfully explored [18,27]. Gold colloid and nanoshells which responded to the light of 532 and 832 nm, respectively, were developed [27]. The independent optical control of microfluidic valves prepared by the hydrogel nanocomposites was achieved via separate irradiation of the two beams [27]. Also, ferrous oxide ( $\text{Fe}_3\text{O}_4$ ) and CNTs generated heat at two very different radiofrequency ranges (296 kHz and 13.56 MHz), which were used to prepare smart SMPCs with multi-shape recovery upon separated radiofrequency actuations [18]. The combination of two materials responsive to different wavelengths enables the “on-demand” shape recovery, overcoming the drawback of conventional triple-shape memory polymer which has to recall its permanent shape following the changing order determined by the programming procedure [28]. To our knowledge, few reports concerned the selective photothermal system within the NIR window. More importantly, as far as micropatterned SMP surfaces are concerned, precise actuation of certain region within the whole pattern before the other area is activated can provide more flexibility of controlling the surface patterned morphologies and correspondingly offer more functions, which has been rarely discussed either.

Furthermore, previous research mainly focused on continuous light irradiation, providing persistent energy input for heat accumulation and temperature increase. Actually, light is not only a form of energy, but can be presented in a signal manner as well. The irradiation of light onto SMPCs can also be achieved in a periodic way with different frequencies, which highly influences the heat accumulation, temperature, and correspondingly the shape recovery behavior of SMPCs. Recently, temperature-memory polymer (TMP) has been reported, the  $T_{sw}$  of which can be controlled by the deformation temperature ( $T_{deform}$ ) [29–32]. One question that arises in this context is whether critical irradiation periodicity and frequency are required to recall the original shape from temporary shape which is deformed at a certain  $T_{deform}$ ? The positive answer may suggest that incorporation of selective photothermal filler into a TMP, producing TMP composites, can realize its response to not merely unique wavelength but to certain irradiation periodicity and frequency, enhancing the “communication” between actuators and operators.

In the present work, a photothermal filler system based on organic rare earth complex is reported to trigger the shape recovery of SMPCs selectively to the NIR light of 980 and 808 nm. More specifically,  $\text{Yb}(\text{TTA})_3\text{Phen}$  and  $\text{Nd}(\text{TTA})_3\text{Phen}$  powders were prepared, while their structures and selective photothermal effects were studied. The two powders were subsequently incorporated into one commercial SMP/TMP of poly[ethylene-*ran*-(vinyl acetate)] (EVA) respectively to prepare the smart SMPCs, enabling the NIR responsive shape recovery to 980 and 808 nm. The effects of irradiation periodicity and frequency on the shape recovery of SMPCs were also examined. Finally, the applications of such SMPCs on the macroscale actuators and micropatterned surface, which can achieve multishaped deformation upon successive irradiations of NIR light of 980 and 808 nm, were demonstrated to prove their versatility.

## 2. Materials and experimental section

### 2.1. Materials

EVA (H2031, VA content = 19%) was obtained from Sumitomo Chemical Company (Japan). Benzophenone (BP, 98%) was purchased from Sigma Aldrich. Triallyl isocyanurate (TAI, 98%) were obtained from Aladdin, China. The  $\alpha$ -thenoyltrifluoroacetone (TTA) and 1,10-phenanthroline (Phen) were purchased from Sinopharm Chemical Reagent Company (China). And  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  were provided by Funing Rare Earth Industrial Company (China). All chemicals were used without further purification.

### 2.2. Preparation of $\text{Yb}(\text{TTA})_3\text{Phen}$ and $\text{Nd}(\text{TTA})_3\text{Phen}$

The synthesized procedures of  $\text{Yb}(\text{TTA})_3\text{Phen}$  and  $\text{Nd}(\text{TTA})_3\text{Phen}$  complexes by co-precipitation method were as follow. The 1 mmol of  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$  or  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ , 3 mmol TTA and 1 mmol Phen were dissolved in ethanol, respectively. Then the ethanol solution of TTA was first added to the three neck flask and it was stirred and refluxed at 60 °C in a water bath. In addition, the  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$  or  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  ethanol solution and the ethanol solution of Phen were added into a three neck flask, successively. The pH value of the reaction mixture was adjusted to 6–7 by dropping 1 mol  $\text{L}^{-1}$  sodium hydroxide ethanol solution. Finally, the mixture was reacted in a 60 °C water bath for 6 h. After the reaction finished, the mixture was centrifuged at the speed of 10000 rpm to obtain the precipitation. The precipitation was centrifuged and washed with water and ethanol, and this process was repeated for three times to obtain the sample, and then the complexes were dried for 12 h in a vacuum oven of 50 °C.

### 2.3. Mixing and UV curing

The mixing and UV curing procedures has been described schematically in a previous report [21]. Solution casting methods were used to fabricate composite films.  $\text{Yb}(\text{TTA})_3\text{Phen}$  or  $\text{Nd}(\text{TTA})_3\text{Phen}$  was introduced into THF respectively and sonicated for 30 min. The EVA pellets, TAI (4 phr) and BP (4 phr) were added into the solution subsequently. The whole solution was stirred vigorously at 60 °C for 1 h. Next, the solution was poured into a Teflon mold, allowing the solvent evaporation naturally for at least 72 h. The obtained film was then placed into a vacuum oven at room temperature for another 24 h. Different powder loadings (2, 5, and 10 phr) were used in this case. The batches were named as  $\text{Yb}(\text{Nd})$ -2,  $\text{Yb}(\text{Nd})$ -5, and  $\text{Yb}(\text{Nd})$ -10, respectively. The obtained film was placed between two glass plates, while the top plate was treated by mold-release agent (Trichloro(1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyl)silane, J&K Chemical, China) and a Teflon film was placed between the

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