Preparation and assembly of five photoresponsive polymers to achieve complex light-induced shape deformations

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HIGHLIGHTS

- Five photoresponsive polymers were prepared and assembled to induce multiple shape deformations.
- The UV light responsive polymer was polyurethane having azobenzene groups in the main chains.
- The other four polymers were crosslinked poly(ethylene-co-vinyl acetate) composites mixing with photothermal fillers.
- The EVA composites recalled their original shapes upon the illuminations merely by the suitable visible and/or NIR light.
- The assembly in three manners improved the spatiotemporal control over shape deformations in a remote manner.

GRAPHICAL ABSTRACT

Five photoresponsive polymers were prepared and assembled in three manners to achieve complicated light-induced shape deformation of polymer specimens, which further expand the applications of light-induced polymers.
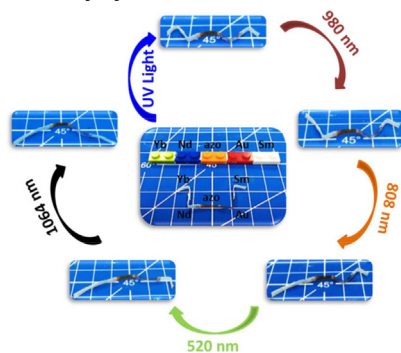
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ABSTRACT

Five photoresponsive polymers towards ultraviolet (UV), visible, and near-infrared (NIR) light were prepared and assembled to achieve complicated light-induced shape deformation. The UV light responsive polymer was contributed by a synthesized linear polyurethane elastomer (azo-PU) containing azobenzene groups in the main chains, which presented both shape-memory effect and UV light-induced shape deformation behavior. The other four polymers that were sensitive to visible or NIR light consisted of crosslinked poly(ethylene-co-vinyl acetate) (EVA) composites mixing with gold nanoparticles (AuNPs), $Nd(TTA)_3Phen$, $Yb(TTA)_3Phen$, and $Sm(TTA)_3Phen$ as photothermal fillers, respectively. The results showed that the shape recoveries of these EVA composites were triggered merely by visible and/or NIR light with suitable wavelengths. Moreover, the assembly of the prepared five light-induced polymers in three different manners improved the spatiotemporal control of complicated shape deformations upon different light illumination sequences. Benefiting from the creation and assembly of five photoresponsive polymers with high wavelength selectivities, complex shapes of polymer specimens can be achieved in a remote and non-contact manner via simply tuning irradiation sequences. The reported materials here and their assembly manners provide a strategy to expand the applications of photoresponsive polymers.

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1. Introduction

Photoresponsive polymers as smart polymeric materials possess an attractive capability to convert light energy into their shape variations and are explored for many applications, including soft actuators, biomedical devices, microfluidic chips, motors, and optical pendulum generators [1–10]. To date, two mechanisms are usually involved in creating photoresponsive polymers. The first efforts are made to prepare photoresponsive polymers on the basis of photomechanical mechanism. As photoisomerizable chromophores, azobenzene moieties which upon light irradiation can photoisomerize between rod-like *trans* and bent *cis* isomers are usually endowed in liquid crystal polymers (LCPs) [10–14]. The accumulation of light-induced structural variations finally contributes to the macroscale shape deformation.

Another majority of the development in light-induced polymers depends on a convenient path of preparing polymer composites containing thermally-induced polymers and photothermal fillers. Such composites can switch thermally-induced shape deformation into a remotely triggered one [15]. Shape-memory polymers (SMPs), as an instance of smart polymers having heat responsiveness, can be precisely programed into pre-defined temporary shapes and recall their original shapes when the temperature goes beyond their switching temperatures (T_{sw}s) [16–20]. The incorporated photothermal fillers in SMP composites (SMPCs) absorb light energy and heat the SMP matrix in a remote, precise, and instant manner [21–24]. Shape recovery is actuated when the indirectly generated temperature reaches T_{sw}.

For each application of photoresponsive polymers, the achievement of complicated or multiple shape deformations of photoresponsive polymers can obviously explore their functions. In nature, complex motion modes of organisms are attributed to their unique motor units, i.e., the combination of simple deformations given by such motor units, including extension, retraction, bending, folding, and twisting, contributes to the on-demand macroscale shape variations or movements. Therefore, the assembly of light-responsive polymers with high wavelength selectivities as the units into a single material system is required to extend shape possibilities upon sequential light illuminations [25–29].

Photoresponsive polymers having wavelength selectivities towards ultraviolet (UV), visible, and near-infrared light are explored based on both photomechanical and photothermal mechanisms over last decades. UV ray, allowing photoisomerization of azobenzene moieties, was involved effectively for LCPs [6,11,12]. Besides, shape recoveries of epoxy-based SMPs were triggered using *p*-aminodiphenylimide or a metallosupramolecular unit as photothermal compounds for UV light [30,31]. Visible light facilitated the photoisomerization of azobenzene moieties with directly modified cores or added substituents in LCPs [32]. Triplet-triplet annihilation-based upconversion luminescence materials were used to convert red light at 635 nm into short wavelength light, indirectly stimulating the prepared cross-linked LCPs containing azotolane [33]. Gold nanoparticles (AuNPs) with surface plasmon resonance mainly played a critical role in altering the shapes of crosslinked poly(ethylene-*co*-vinyl acetate) (EVA) and poly(ethylene oxide) as thermally-induced SMPs particularly for green light [21]. Three colored inks as hinges were used to absorb the distinguishable visible light (red: 660 nm, green: 530 nm, and blue: 470 nm) and as a result to induce the folding of certain regions on a commercial SMP film [26].

The primary advantage of near-infrared light over UV and visible lights is the safety for human tissues and naked eyes. Another upconversion material of $NaYF_4$ nanoparticles, converting the NIR light at 980 nm into short wavelength light, also aided the shape deformation of cross-linked LCPs containing azotolane [34]. The widely reported photothermal fillers suitable for NIR lights, on the other hand, mainly consisted of carbon-based nanomaterials [35,36], which can also be heated using UV light [30], visible light [37], microwave [38], or even radio frequency wave [39,40]. Recently, we reported Yb^{3+} and Nd^{3+} based rare-earth organic complexes as selectively photothermal fillers for the NIR light at 980 and 808 nm, respectively [41,42]. Via physical mixing or in-situ copolymerization, NIR light responsive crosslinked EVA or poly(methyl methacrylate) composites were prepared separately. The conjoined and bilayer assembly strategies were also preliminarily demonstrated.

As far as the assembly approach of photoresponsive polymers is concerned, the homogeneous incorporation of photothermal fillers into LCPs having photomechanical responsiveness was addressed as one combination procedure [25]. The initial exposure to UV light resulted in film bending before shape recovery occurred upon subsequent exposure to NIR light. In addition, the heterogeneous construction methods can be divided into three manners. First, Yang et al. explored a new assembly strategy to fabricate a polymer film with two active layers, which can present reversible bending and chiral twisting under the irradiations of UV and NIR light [28]. Second, creation of photoresponsive units as hinges onto photo-inert polymer films or utilization of light absorber as hinges onto thermally-induced polymer films were reported as well [26,27,43]. The third approach is to conjoin responsive polymer specimens one by one, while the adjustment of irradiation sequences can switch the deployment order of a temporary zigzag shape [30,39]. Yang et al. used *p*-aminodiphenylimide and multi-walled carbon nanotubes (CNTs) as selective photothermal fillers for UV and NIR light in epoxy as thermally-induced SMP. Complicated shape deformations were achieved via irradiating different light onto the conjoined epoxy composites [30].

In recent advances, however, at most three photoresponsive polymers were usually assembled and as a result merely three kinds of light were involved to our best knowledge. In our childhood, we learned that more toy bricks we can collect, more complex shapes and structures we can construct. Therefore, one main challenge here still lies in the enrichment of photoresponsive polymers with high wavelength selectivities.

Here, we prepared five photoresponsive polymers for UV, visible, and NIR light, respectively, as well as assembled them in three different manners to improve the spatiotemporal control over shape deformations upon different light irradiations. While the UV light responsive polymer consisted of a linear polyurethane elastomer containing azobenzene groups in the main chains, the remaining visible or NIR light-induced polymers were all prepared based on crosslinked EVA as a thermally-induced SMP, which were blended with photothermal fillers of gold nanoparticles (AuNPs), $Nd(TTA)_3Phen$, $Yb(TTA)_3Phen$, and $Sm(TTA)_3Phen$, respectively. The five polymers were named as azo-PU, EVA-Au, EVA-Nd, EVA-Yb, and EVA-Sm for simplicity. To facilitate the understanding, the selected materials, including the synthesized polyurethane and the prepared EVA composites, are shown diagrammatically in Fig. 1. We investigated the light-induced shape
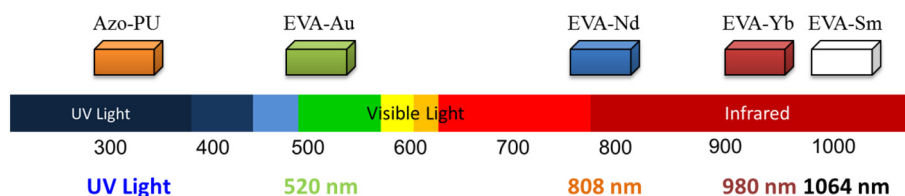

Fig. 1. Schematic diagram of the selected EVA composites and the polyurethane material with wavelength selectivities (Azo-PU: UV light; EVA-Au: 520 nm; EVA-Nd: 808 nm; EVA-Yb: 980 nm; EVA-Sm: 1064 nm).