

# Near-infrared responsive soft actuators consisting of thermosensitive hydrogels and photothermal conversion lanthanoids with wavelength selectivity

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Near-infrared responsive soft actuators have attracted much attention for applications to microsystems in bioliving. However, conventional photothermal conversion systems using carbon materials allow only for the actuation at millimeter scales because of the accuracy of beam irradiation spots. We have focused on imparting wavelength selectivity to photothermal conversion materials. By incorporating several wavelength-selective materials into different positions of the actuator, the desired location is moved simply by irradiating whole actuators and switching the wavelength of the light. In this study, we fabricated soft actuators consisting of thermosensitive hydrogels and photothermal conversion lanthanoid materials with narrow adsorption bands in near-infrared regions. Nd<sup>3+</sup> and Yb<sup>3+</sup> were used as absorbers at 808 nm and 980 nm, respectively. These lanthanoid materials were incorporated as nanoparticles and coordinated molecules in poly(*N*-isopropylacrylamide thermosensitive hydrogels. 808 nm and 980 nm irradiation gave shrinkage and bending motion of the Nd<sup>3+</sup> and Yb<sup>3+</sup> parts on the gels, respectively at room temperature. After turning off the light, the gels returned to their original shapes. No deterioration of the actuator was observed even after repeated experiments.

Key words: soft actuator, near-infrared light, wavelength selectivity, lanthanoid, photothermal conversion

## 1. INTRODUCTION

Near-infrared controlled soft actuators have attracted much attention for medical applications, such as artificial muscles [1], micromachines [2], and micro total analysis systems [3], because the actuators are lightweight, soft, and contactless, and contain no electric circuits or batteries. Near-infrared light has been converted into mechanical force through radiation force [4] and photothermal conversion [5]. Photothermal conversion systems offer good energy conversion efficiency, enabling the actuators to operate at low power. These soft actuators typically consist of thermosensitive polymers and photothermal conversion fillers. Thermosensitive polymers include thermal expansion silicone elastomers [6] or thermally shrinkable hydrogels [7]. Carbon nanomaterials were often used as photothermal conversion fillers. [5] The actuators were motioned by irradiating near-infrared light at the points of the gels where you want to move. However, the size of the actuators was limited to the millimeter scales because of the accuracy of irradiation beam spots.

We have developed the strategy to replace the conventional technique using illumination position with the new technique using material patterning position. The new technique involves irradiating the entire actuator with near-infrared light and patterning the photothermal conversion material locally. Two or three

kinds of photothermal conversion materials with different wavelengths and narrow adsorption bands were patterned in each different position of the actuators. By switching the wavelength only, it was possible to move individual parts of the actuator. The lanthanoids were selected from among wavelength-selective materials such as dyes [8], gold nanomaterials [9], and lanthanoids [10] because they have the narrowest absorption band, excellent heat resistance, and easy to adjust size of the materials. Here, we demonstrate bending-type soft actuators consisting of thermosensitive hydrogels and lanthanoid materials which were incorporated as nanofillers or molecular clusters.  $\text{Nd}^{3+}$  and  $\text{Yb}^{3+}$  were selected as an 808 nm- ( $^4\text{F}_{9/2}-^2\text{H}_{9/2}$  and  $^4\text{F}_{9/2}-^4\text{F}_{5/2}$  transitions of  $\text{Nd}^{3+}$ ) and 980 nm- ( $^2\text{F}_{7/2}-^2\text{F}_{5/2}$  transition of  $\text{Yb}^{3+}$ ) light absorber, respectively. [10]

## 2. INTRODUCING LANTHANIDS INTO GELS AS A FILLER

Lanthanoid materials can be designed into various sizes because the absorption wavelength and molar extinction coefficient absorbance of lanthanoids do not depend on the solid size. In addition, the photothermal conversion efficiency is necessarily high because lanthanoids usually do not have high luminous efficiency. The advantage of the nanoparticle form is easy combination with gels because of no requirements of chemical modification to the gels, and complex process to mix. The 100 nm size lanthanoid nanoparticles were used. The procedure was followed according to previous work [11] and shown in Figure 1. The block-rod gels containing locally arranged particles were prepared by step-wise polymerization in glass capillaries. Glass capillaries with a diameter of 1 mm were half-filled with a  $\text{Nd}_2\text{O}_3$ -particle aqueous dispersion ( $8 \text{ mg mL}^{-1}$ ) containing 0.7 M N-isopropylacrylamide, 0.035 M (5 mol%) N, N-methylenebisacrylamide, and 0.007 M 2,2-diethoxyacetophenone (1 mol%). The samples were photopolymerized by exposure to ultraviolet light at the same conditions as above. Before polymerization, the capillaries were allowed to stand for 24 hours to precipitate  $\text{Nd}_2\text{O}_3$  particles on the bottom of the capillaries by gravitational force to convert the volume phase transition into bending motion. The space next to the  $\text{Nd}_2\text{O}_3$ -rod gels in the capillaries was then filled with a  $\text{Yb}_2\text{O}_3$ -particle dispersion ( $8 \text{ mg mL}^{-1}$ ) containing the same monomer precursors. The capillaries were rotated for the  $\text{Yb}_2\text{O}_3$  particles to precipitate on the same or opposite side to the  $\text{Nd}_2\text{O}_3$  particles. After precipitation of the  $\text{Yb}_2\text{O}_3$  particles for 24 h, photopolymerization of the samples was performed. The block-rod gels were shrunk by heating at  $50^\circ\text{C}$  and then taken out of the capillaries.

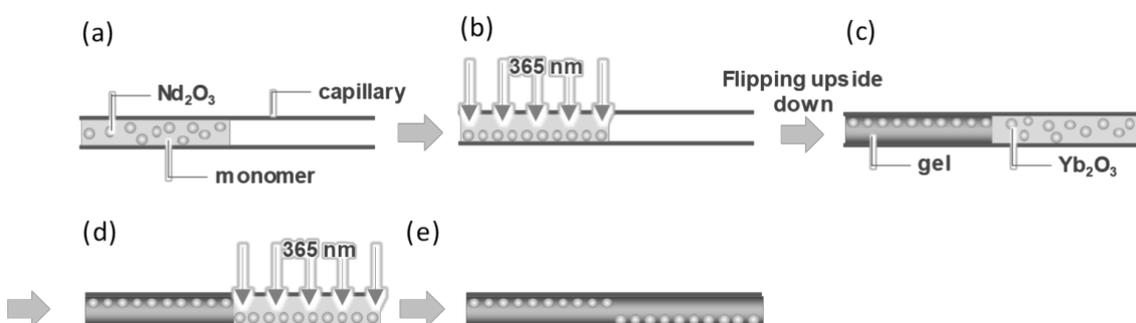


Figure 1. Schematic of fabrication of lanthanoid-particle-precipitated rod gels for bending motion. Fabrication of the (a, b)  $\text{Nd}_2\text{O}_3$ -particle-gel moiety, (c, d)  $\text{Yb}_2\text{O}_3$ -particle-gel moiety, and (e) final rod gels

with  $\text{Nd}_2\text{O}_3$ - and  $\text{Yb}_2\text{O}_3$ -particle-precipitated moieties.

The gel volume can be changed over about  $35\text{ }^\circ\text{C}$  due to the volume phase transition of poly(*N*-isopropylacrylamide). The irradiation of near-infrared light led to an increase in gel temperatures due to the absorption of the light from lanthanoids and emitting of the thermal energy, resulting in the shrinkage of the gels. To induce the volume phase transition, many factors should be considered, such as the light irradiation intensity, rare-earth particle concentration, and water temperature of the gels. We have optimized the experimental conditions to occur volume phase transition with wavelength selectivity. The optimized water temperature and light intensity were at  $28\text{ }^\circ\text{C}$ , and  $3\text{ W cm}^{-2}$ , respectively.

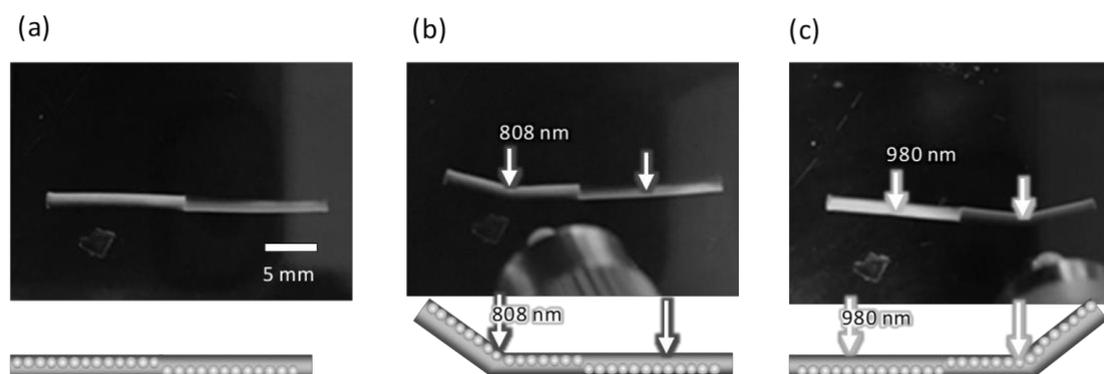


Figure 2. Photographs of a rod gel with (a) no irradiation, and (b) 808 and (c) 980 nm near-infrared light irradiation at  $3\text{ W cm}^{-2}$  for 60 s at  $28\text{ }^\circ\text{C}$ . The left and right sides of the 1-mm-diameter rod gel are the  $\text{Nd}_2\text{O}_3$ - and  $\text{Yb}_2\text{O}_3$ -particle-precipitated gel moieties, respectively. For ease of photographing, the position of the settled particle part in the rod gel in (c) was inverted concerning that in (a) and (b).

Figure 2 shows a visual observation photograph of the wavelength-selective bending of a rod gel. Bending of the rod gel by about  $30^\circ$  occurred at the irradiation points for both sides as a photo steady state when the  $\text{Nd}_2\text{O}_3$  and  $\text{Yb}_2\text{O}_3$  moieties were irradiated at 808 and 980 nm, respectively. Irradiation with the correct wavelength light led to the bending of any part of the gels. The irradiation points immediately started to turn turbid white. The rod gel then began to bend and reached a steady bending state in less than 10 s. When the irradiation was turned off, the white turbidity promptly disappeared and the gel rod gradually returned to its original shape within several minutes. The opposite combination of absorption band mismatch showed no change, even for irradiation for several minutes.

The principle of rod gel bending was as follows. The gels only shrank if the entire rod gel was heated. When only one side of the gel shrank selectively, the gels bent toward the shrink direction. The Heating energy generated on the lanthanoid side of the gels caused the volume phase transition in the surroundings, but not on the other side. This may be due to that the heating energy was dissipated to the surroundings during the process of transferring to the other gels.

### 3. INTRODUCING LANTHANIDS INTO GELS AS A MOLECULAR

Mixing fillers often causes problems with turbidity and solidification due to light scattering and aggregation. Next, we have incorporated lanthanoids into the gels as a molecular. We fabricated an interpenetrating gel of poly(*N*-isopropylacrylamide) and sodium polyacrylate to immobilize lanthanide ions in the gel network. The interpenetrating gels would be expected to prevent the excess cross-linking of the entire gel network by lanthanoid ions in comparison to copolymerization gels.

The interpenetrated gels were prepared according to the procedure in Figure 3 and previous work [12]. The poly(*N*-isopropylacrylamide) precursor consisted of a solution of 700 mM *N*-isopropylacrylamide, 3.5 mM *N, N'*-methylenebisacrylamide, and 0.07 mM 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone in water. The precursor was deoxygenated by nitrogen bubbling in a sealed vial for 1 h. In a nitrogen glove box, quartz cells were filled with the precursor. The cells were exposed to ultraviolet light from a blacklight lamp at 360 nm and  $0.1 \text{ mW cm}^{-2}$  on a cooled table at about 5 °C for 24 h. The cells were removed to obtain the transparent gels. The gels were dried in a vacuum and then added to a sodium acrylate precursor at about 5 °C for 24 h. The sodium acrylate precursor was prepared by neutralizing 0.7 M acrylic acid solution with 1.0 M sodium hydroxide solution and adding 0.07 mM 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone. The sodium acrylate precursor was deoxygenated in the same manner as above. The poly(*N*-isopropylacrylamide) gels were swelled with the sodium acrylate precursor and polymerized with ultraviolet irradiation in the same manner as above to obtain the transparent interpenetrate gels. The gels were immersed in a solution of 0.2 M neodymium or 0.2 M ytterbium ions at about 5 °C for 24 h. The immobilization of the lanthanoid ions caused the gels to become turbid. The gels were removed from the solutions and were washed with water several times.

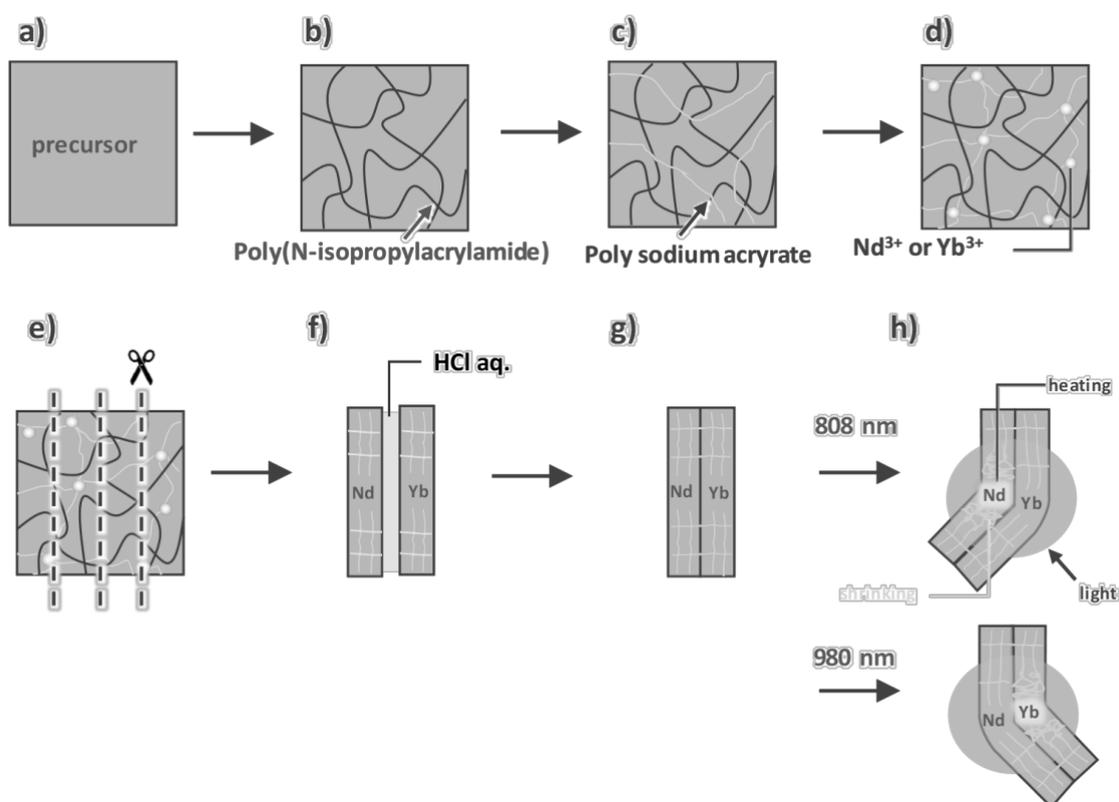


Figure 3. Schematic of the preparation of interpenetrated gels. (a) poly(*N*-isopropylacrylamide) precursor solution, (b) formation of poly(*N*-isopropylacrylamide) gel by photo radical polymerization, (c) formation of interpenetrated gel by immersion in an sodium acrylate precursor solution and photo radical polymerization, (d) formation of a lanthanoid-coordinated gel by immersion in solution, (e) gel rods cut with a knife, (f) adhesion of a Nd<sup>3+</sup>-coordinated rod gel and a Yb<sup>3+</sup>-coordinated rod gel with a small droplet of HCl solution, and (g, h) a two-wavelength selective-response soft actuator. (h) Irradiation of the actuator with near-infrared light at 808 and 980 nm.

Figure 4 shows photographs of the actuators in water at 25 °C before and during near-infrared irradiation at 808 and 980 nm for 5 min. The actuators were strong enough to maintain the adhesion between the Nd and Yb gels in water for several months. Near-infrared irradiation at 808 nm induced a bending motion in the actuator toward the Nd<sup>3+</sup> gel side. The bending angle of the actuator reached about 38°. Near-infrared irradiation at 980 nm induced a bending motion in the actuators toward the Yb<sup>3+</sup> gel side. The bending angle reached 30°. Both bends of the actuator took about 4 minutes. Turning the light off allowed both bent actuators to return to their original shape within a few minutes. It takes several hours for it to fully recover. Because water absorption of the gel took longer than dehydration, the activation energy for the rearrangement of water and gel was higher for water absorption than for dehydration. The actuators reproduced the bending motions under light irradiation and the return motion in the dark after irradiation. Repeated experiments did not damage the actuators.

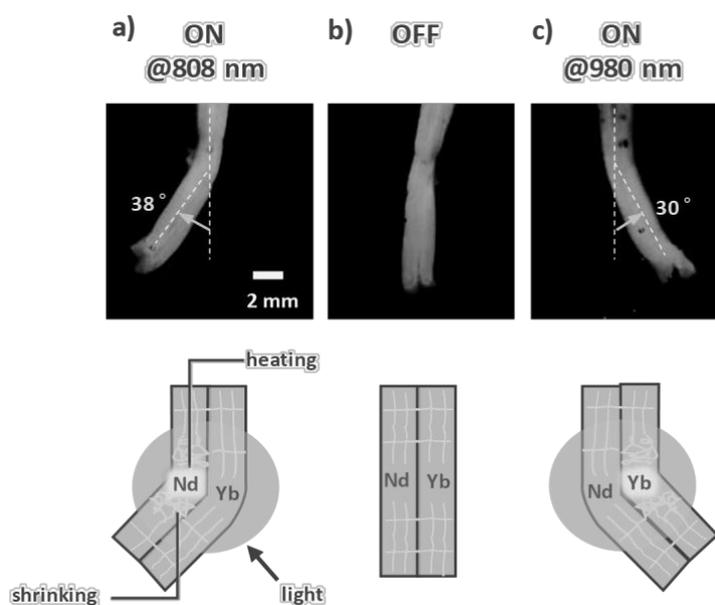


Figure 4. Photograph of a soft actuator consisting of  $\text{Nd}^{3+}$  and  $\text{Yb}^{3+}$ -coordinated gels in water at 25 °C in (b) the dark and under near-infrared light irradiation at (a) 808 and (c) 980 nm at  $2.5 \text{ W cm}^{-2}$  for 5 min. The center of the laser light was the center of the photograph. (d) Bending angle plotted with time of the above data.

### 3. CONCLUSION

We demonstrate the fabrication of soft actuators consisting of thermosensitive hydrogels and lanthanoid materials. This concept can be generalized to design remote control soft actuators. Generally, there is a trade-off between the wavelength selectivity and the photothermal conversion efficiency and it is required to carefully select and optimize the wavelength-selective materials for purpose. Conventional fabrication techniques such as photolithography, soft lithography, and printing enable the fabrication of soft actuators at micro scales. This report paves the way for noncontact remote micromachines. The potential applications of the systems are wide, including biological and medical applications using “near-infrared windows”, remote control of the valves of microflow systems, sub-micro-scale mass transportation systems, and self-propelling micromachines.

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