



Shape-shifting composite hydrogel sheet with spatially patterned plasmonic nanoparticles

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Complete List of Authors:	Guo, Hongyu; University of Maryland, College Park, Liu, Yijing; National Institute of Biomedical Imaging and Bioengineering Yang, Yang; University of Maryland, College Park Wu, Guangyu; University of Maryland, College Park; Harbin Institute of Technology, School of Chemistry and Chemical Engineering DeMella, Kerry; University of Maryland, Chemical and Biomolecular Engineering Raghavan, Srinivasa; University of Maryland, Chemical and Biomolecular Engineering Nie, Zhihong; University of Maryland, Department of Chemistry and Biochemistry



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Shape-shifting composite hydrogel sheet with spatially patterned plasmonic nanoparticles

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Hongyu Guo^a, Yijing Liu^b, Yang Yang^a, Guangyu Wu^{a,c}, Kerry Demella^d, Srinivasa R. Raghavan^d and Zhihong Nie^{a*}

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We reported a simple and reliable approach to fabricate composite hydrogel sheets with spatially patterned regions of plasmonic gold nanoparticles using the combination of contact printing and diffusion-controlled galvanic replacement reaction. In response to near-infrared laser irradiation, the localized increase in temperature induced the controlled shape deformation of the composite hydrogels, due to the combination effect of photothermal heating of loaded gold nanoparticles and thermal responsiveness of hydrogel matrix. The same hydrogel can be designed to exhibit different modes of shape deformations depending on the direction of light irradiation, which has rarely been reported previously. The composite hydrogels may find applications in biomedicine and soft robots.

Shape-changing materials have attracted considerable attention in the past decades, owing to their potential applications in soft robot, artificial muscle, biomedicine and mechanical device.^[1-9] Among these materials, hydrogel, a water-swollen network, is unique since its deformation usually relies on a differential swelling in the material, which mimics naturally occurring shape-changing objects, such as tendril, pine cone, Venus flytrap, etc.^[1-2, 7] Common strategies to generate differential swelling in hydrogels include layering materials that have varying swelling capability or generating domains within hydrogel that have swelling extent different from their surrounding materials.^[1, 7-8] Many environmental stimuli have been used to induce differential swelling in the hydrogel to trigger its deformation, such as temperature,^[10-12]

pH,^[13] ionic strength,^[14] enzyme,^[15] DNA,^[16] ions,^[17] humidity,^[18-19] light^[20-22] and external fields.^[23-24] Among others, light is particularly attractive as it can be remotely delivered to material with desirable spatial and temporal resolution, which brings more controllability to the shape transformation of materials, such as liquid crystal polymer/elastomer,^[25-34] shape memory film,^[35-37] supramolecular assembly,^[38-39] and hydrogel.^[20-21, 40-45] For example, light can be used to drive the transformation of the same hydrogel sheet into multiple distinct shapes by modulating light irradiation patterns,^[40-41] which cannot be readily achieved by using chemical-responsive hydrogel.^[46-47] Controllable motion of shape-changing hydrogel can be realized by region-selective exposure of materials to light to induce shape deformation.^[43-44] Despite the shape-transformation versatility enabled by local irradiation of light in these platforms, this strategy often requires a special set-up or is limited by undesired shape transformation originated from variation in the irradiation area upon the deformation of materials.^[41]

Instead of modulating area of light exposure, one can structure the materials with light-responsive components and use un-patterned light to control the shape transformation of the material. This concept has been extensively used in the deformation of azobenzene-based materials in which azobenzene moiety is pre-patterned in the materials, thus enabling defined deformation under light.^[31, 48] Another example is the shape transformation of pre-strained polystyrene film where the regions patterned with colored inks serve as actuation hinges in response to light.^[37] In this case, the spatial distribution of the light responsive components is crucial to the mode and complexity of the shape transformation of materials.^[37] However, there remains challenging to readily control the distribution of light-responsive elements in materials simultaneously along both in-plane and axial direction, in order to achieve more complex shape transformation modes.

Herein we reported a simple and reliable strategy to fabricate shape-transforming composite hydrogel sheets that

^a Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, 20742, USA. E-mail: znie@umd.edu

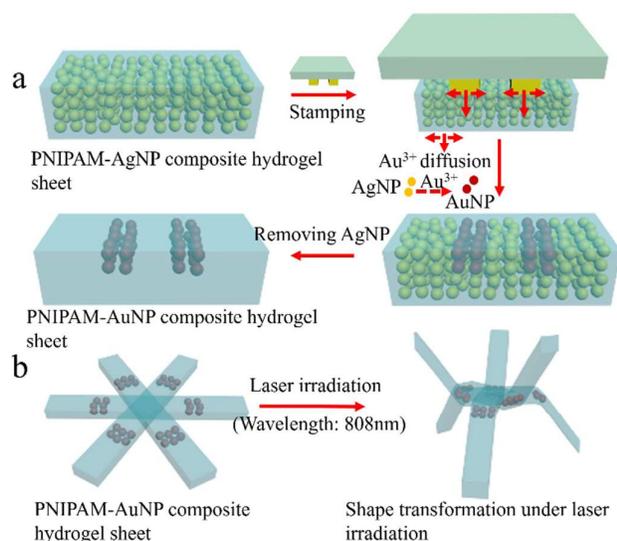
^b Laboratory of Molecular Imaging and Nanomedicine (LOMIN), National Institute of Biomedical Imaging and Bioengineering (NIBIB), National Institutes of Health, USA

^c MIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, State Key Laboratory of Urban Water Resource and Environment, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China

^d Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD, 20742, USA

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are integrated with light-responsive domains with controlled distributions in both lateral and z-direction of a thermo-responsive hydrogel. The approach was based on contact printing of gold ion into a hydrogel sheet pre-embedded with spherical silver nanoparticles (AgNPs) that have absorption in the visible range and subsequent diffusion-controlled galvanic replacement reaction between gold ions and AgNPs to produce hollow gold nanoparticles (AuNPs) with near-infrared (NIR) absorption (Scheme 1). After removing unreacted AgNPs, the resulting AuNPs were retained in the hydrogel. This approach allows us to control the distribution of light-responsive domains (i.e., photothermal contrast agent of AuNPs) in both lateral and z-direction of the hydrogel matrix by modulating the gold ion diffusion. The composite hydrogel exhibits distinct deformation modes upon NIR light irradiation, depending on irradiation direction and spatial distribution of AuNP domain. This shape-transforming scenario has rarely been reported previously.



Scheme 1 a) Schematic illustration of patterning plasmonic AuNPs in both lateral and z-direction of the thermo-responsive hydrogel matrix. b) NIR light-induced deformation of 2D composite hydrogel sheet patterned with photothermal contrast agent (i.e., AuNPs) into 3D geometry.

In brief, an agarose hydrogel stamp pre-soaked in a gold ion solution was brought in conformal contact with AgNP-embedded hydrogel matrix. The AgNP-loaded composite hydrogel matrix was prepared by redox polymerization of an aqueous mixture containing AgNPs, N-Isopropylacrylamide (NIPAM) monomer, N,N-Methylenebis(acrylamide) cross-linker, ammonium persulfate, and N,N,N',N'-Tetramethylethylenediamine (TEMED) catalyst (see SI for details). The number density of AgNP in the original hydrogel is estimated to be $5.6 \times 10^{11} / mL$ (see SI for calculations). As the stamp contacted the composite hydrogel, gold ion diffused into the composite hydrogel via a concentration-driven diffusion mechanism. During gold ion diffusion, the galvanic replacement reaction between gold ion and AgNPs regioselectively turned AgNPs into AuNPs *in situ* within the

hydrogel. The unreacted AgNPs were subsequently etched away by using an aqueous solution of $NH_3 \cdot H_2O$ and H_2O_2 as wet etchant, leaving AuNPs in the hydrogel. Various patterns with desired feature size (~ 500 micron) and spacing ($\sim 1mm$) were generated by using this approach with the potential of further increasing its resolution (see Fig. 1a-d). The high edge resolution in the AuNP patterns is evidenced by the sharp light intensity transitions between AuNP-containing and AuNP-free regions (see inset graphs in Fig. 1a-d). This approach could be readily scaled up. A 2cm by 2cm array of AuNP dots was patterned in the hydrogel to demonstrate the scale-up potential of this approach (see Fig. S1). The AuNPs generated by the galvanic replacement reaction had hollow porous structures,^[49] as evidenced by SEM characterization (Fig. 1e). After reaction, the AuNP-containing composite hydrogel showed broad light absorption in the NIR range (Fig. 1f), presumably due to varied morphologies of resulting porous hollow AuNPs in the gel (Fig. 1e). In contrast, the original AgNP-loaded gel exhibited a lower absorption in the NIR range due to the solid spherical morphology of AgNPs (Fig. 1f, Fig. S2).

The unique feature of our approach to pattern AuNP in hydrogel is that the AuNP domain size in both lateral and z-direction of the hydrogel can be controlled by varying stamping time and $HAuCl_4$ precursor concentration (Fig. 2). Fig.2a-c clearly indicated the variation of AuNP domain size with respect to $HAuCl_4$ concentration in both lateral and z-direction of the hydrogel, demonstrating the excellent control over the spatial distribution of AuNP domains in hydrogel. The pattern depth and width of AuNPs can be controlled by varying the $HAuCl_4$ precursor and stamping time (Fig. 2d,e). For instance, the depth and width of AuNP domains increased from $660\mu m$ to $880\mu m$ (Fig.2d) and increased from $260\mu m$ to $360\mu m$ (Fig.2e), with increase of stamping time from 1 minute to 2 minutes at a $HAuCl_4$ concentration of 10mM. Such fine control over AuNP domain size in the z-direction of material by using the diffusion-controlled method cannot be readily achieved by other approaches such as microcontact printing^[50] and photon lithography.^[51]

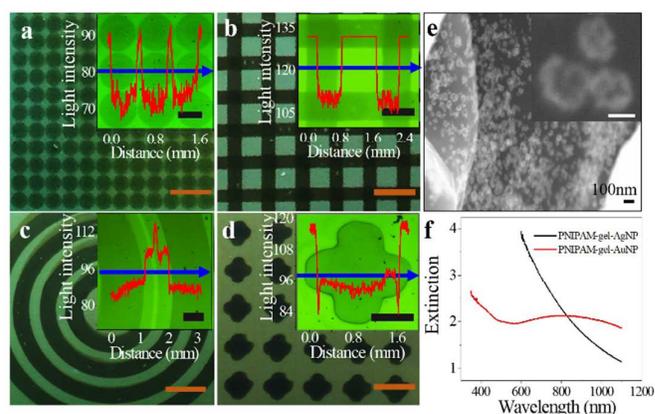


Fig. 1 a-d) Composite hydrogel sheet patterned with plasmonic AuNP regions of different shapes by stamping approach. Insets are optical microscopic images of the

patterns and light intensity profiles of the patterned domains along direction as indicated by blue arrow. e) SEM image of generated AuNPs with porous hollow feature. f) UV-Vis spectra of hydrogel hybrid before (black curve) and after stamping (red curve). Scale bars are 2mm in (a-d) and 0.5mm in insets of (a-d), and 40nm in inset of (e).

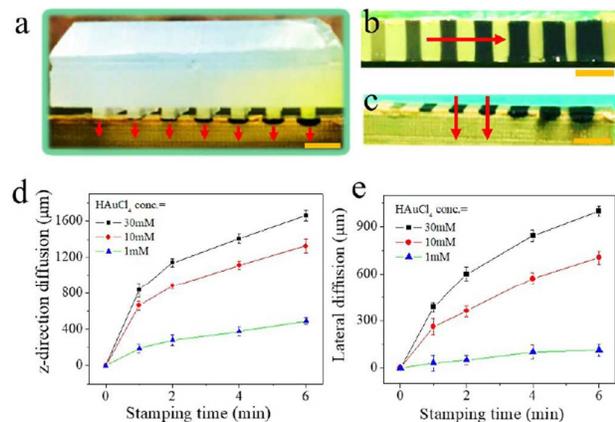


Fig. 2 Analysis of diffusion-reaction process during stamping. a) The contact printing of stamp soaked with gold ion solutions of different concentrations (increasing from left to right) on hydrogel sheet. The red arrows indicate the propagation direction of AuNP domain along thickness direction of sheet. b, c) Top view (b) and side view (c) of the hydrogel after stamping. Arrows indicate the direction of increasing density or size of Au NP domains generated in the hydrogel; d, e) Time-dependent variation of AuNP domain size in z-direction and lateral direction of the hydrogel. Scale bars are 2mm in (a-c).

The AuNP-patterned hybrid hydrogel sheet transformed to 3-D geometries under 808 nm laser irradiation, due to localized shrinkage of the thermo-sensitive composite hydrogel arising from the photothermal heating of AuNPs.^[42, 52-54] The deformed hydrogel returned to its original state in 2 minutes after removing the laser (see Fig. S3b). The bending/recovering could be repeated for many times without appreciable change in bending angle, demonstrating high reversibility of the deformation (see Fig. S4).

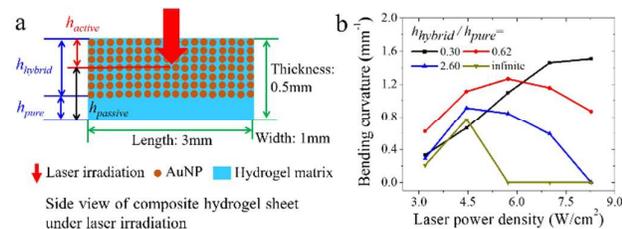


Fig. 3 a) Schematic illustration of the cross-section of the composite hydrogel sheet under laser irradiation. b) Bending analysis of the composite hydrogel sheet as a function of laser power density.

To study its bending behaviour as a function of laser power density (PD), the composite hydrogel sheet was patterned to have a bilayer-type structure as illustrated in Fig. 3a. Here the bilayer sheet consists of a hybrid gel layer (containing AuNP domain) with a thickness of h_{hybrid} and a pure gel layer (without AuNPs) with a thickness of $h_{passive}$ (Fig.3a). As shown in Fig.3b, when $h_{hybrid}/h_{pure}=0.3$, the bending curvature of the composite hydrogel sheet increased with increase of PD. When $h_{hybrid}/h_{pure} \geq 0.6$, the bending curvature exhibited a peak

as a function of laser PD. These bending behaviours can be explained by using the classical model developed for bending deformation of bi-metal thermostats. The bending curvature of hydrogel sheet (κ) is described as,^[55-56]

$$\kappa = 6 \frac{eh(1+h)\Delta\xi}{h_{total}(1+4eh+6eh^2+4eh^3+e^2h^4)}$$

where h_{total} , e , h and $\Delta\xi$ are thickness of composite hydrogel sheet, ratio between Young's modulus of active and passive gel layer, ratio between thickness of active and passive gel layer and actuation force, respectively. Here the actuation force is the volumetric swelling ratio difference between active and passive gel layer. This model has been used previously to interpret bending of shape-changing hydrogel material.^[16, 57]

We note that the magnitude change of e during laser irradiation does not produce substantial effect on bending curvature of the composite hydrogel sheet (see SI for calculation details). This observation is in a good agreement with our prediction by the model and conclusion drawn in previous report^[56] (see more detailed discussion in Supplementary Information). Therefore, we consider e as a constant and study effects of h and $\Delta\xi$ on bending curvature of the composite hydrogel sheet in the following discussion.

In the bending deformation of our composite sheet, the active gel layer is the layer that absorbs light and generates heat, while the passive gel layer is the layer that does not absorb laser energy (Fig.3a). Due to laser intensity decay (caused by strong absorption of AuNPs in the hydrogel sheet) along irradiation direction, thickness of active and passive gel layer (h_{active} , $h_{passive}$, Fig.3a) varied depending on thickness of hybrid gel layer and laser PD. When $h_{hybrid}/h_{pure}=0.3$, light can access all the hybrid gel layer. In this case, since $h=h_{active}/h_{passive}=0.3$ ($h_{active}=h_{hybrid}$, $h_{passive}=h_{pure}$) is a constant, the increase in laser PD led to an increase in $\Delta\xi$ (see Fig. S5b) and hence increase in bending curvature. In contrast, at high h_{hybrid}/h_{pure} , light can only penetrate part of the hybrid layer due to strong light absorption by AuNPs and intensity decay along hydrogel's thickness direction. The light penetration depth increased with increase of laser PD, leading to an increase of $h=h_{active}/h_{passive}$. As a result, the dependency curve of bending curvature on laser PD exhibited a parabolic form.^[57] The bending curvature was found to increase with decreasing gel thickness (see Fig. S6, Fig. S7). The result is in a good agreement with the model, since a smaller h_{total} of thinner gel gives rise to a larger κ when other parameters (h , e and $\Delta\xi$) are the same.

We note that the surface temperature of pure PNIPAM hydrogel only slightly increased upon laser irradiation, thus leading to negligible deformation of the hydrogel (Fig. S8 and S9a). In contrast, hybrid PNIPAM hydrogel heated up substantially and bent appreciably under the same condition of laser irradiation (Fig. S8 and S9b). These results suggest that the presence of hybrid layer in the composite hydrogel plays a central role in its shape transformations.

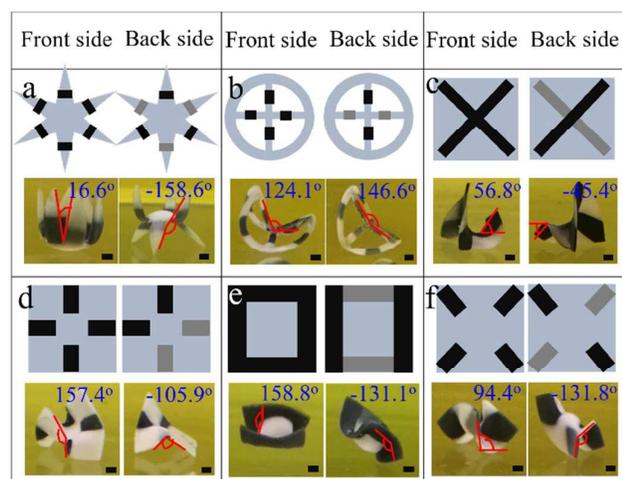


Fig. 4 Shape deformation of patterned composite hydrogel sheet under a continuous laser irradiation (wavelength: 808nm). The black and grey regions represent areas with AuNPs patterned throughout the hydrogel and partially into the hydrogel along thickness direction, respectively. The negative bending angle indicates a bending direction was opposite when laser was irradiated onto the hybrid hydrogel from different sides (front side vs. back side). The total thickness (h_{total}) of composite hydrogel sheet and thickness of hybrid gel layer (h_{hybrid}) are: (a) $h_{total}=0.25\text{mm}$, $h_{hybrid}=0.18\text{mm}$; (b) $h_{total}=0.50\text{mm}$, $h_{hybrid}=0.46\text{mm}$; (c) $h_{total}=0.25\text{mm}$, $h_{hybrid}=0.23\text{mm}$; (d) $h_{total}=0.25\text{mm}$, $h_{hybrid}=0.08\text{mm}$; (e) $h_{total}=0.25\text{mm}$, $h_{hybrid}=0.22\text{mm}$; (f) $h_{total}=0.25\text{mm}$, $h_{hybrid}=0.18\text{mm}$, respectively. A laser power density of $6.38\text{W}/\text{cm}^2$ was used in all cases. Scale bars: 1mm.

Finally, we fabricated composite hydrogel sheets with varied AuNP patterns (Fig. 4). In these composite sheets, AuNPs were patterned throughout the hydrogel in certain region (colored black in illustrations in Fig.4) and partially into the hydrogel in other region (colored grey in illustrations in Fig.4) along hydrogel's thickness direction. For simplicity in discussion, we defined "front side" of the hydrogel as the side that has more AuNP domains and the "back side" as the side that has smaller number of AuNP domains. As an example, the "front side" of star-like composite sheet has six AuNP domains while its "back side" has three AuNP domains (Fig.4a).

We found that the patterned composite hydrogel sheet had distinct deformation behaviours, depending on which hydrogel side was irradiated (Fig. 4). As an example, when "front side" of the patterned star-like hydrogel sheet was irradiated, all six petals bent to same direction; while they bent to opposite directions when its back side was irradiated (see Fig.4a and SV1,2). This is because when irradiated from "back side" of the star-like hydrogel sheet, the three petals with AuNP domains on this side bent towards laser while the other three petals bent away from laser since the AuNP domains were located on their "front side". The deformations of composite sheet with other AuNP patterns are affected by light exposure direction as well (Fig.4b-f). For example, when "front side" was irradiated, the square-shaped composite hydrogel sheet with AuNP patterned on its corner transformed to a saddle geometry; while it deformed to an incomplete tube-like structure when its "back side" was irradiated (Fig.4f). As far as we know, this deforming scenario has not been reported previously.

Conclusions

We reported a simple and reliable approach to pattern photothermal contrast agents (i.e., AuNPs) spatially in a thermo-responsive hydrogel matrix by using contact printing of metal precursors and galvanic replacement of AgNPs pre-embedded in the hydrogel matrix. The distribution of AuNPs in both lateral and z-direction of the hydrogel can be controlled by varying the diffusion and reaction of stamped chemicals. The composite hydrogel sheet transformed to 3-D geometries under a continuous NIR laser irradiation by the combination of photo-thermal effect of AuNPs and thermo-responsive property of the hydrogel matrix. This approach allowed us to design composite hydrogel that exhibited distinct transformation modes, depending on laser irradiation direction, which has rarely been reported previously. We foresee that the patterning technique reported here is general and can be applied to other thermo-responsive hydrogel systems, while the patterned composite hydrogel may find applications in biomedicine^[10, 58] and soft robotics.^[17, 21-22]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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TOC

Shape-shifting Composite Hydrogel Sheet with Spatially Patterned Plasmonic Nanoparticles

Hongyu Guo, Yijing Liu, Yang Yang, Guangyu Wu, Kerry Demella, Srinivasa R. Raghavan and Zhihong Nie*

A simple and reliable approach was developed to fabricate thermo-responsive composite hydrogel sheet with spatially patterned regions of plasmonic gold nanoparticles. The same hydrogel exhibited different modes of shape deformations under near-infrared laser irradiation depending on irradiation direction.

