**Abstract:** Patterning deformation within the plane of thin elastic sheets represents a powerful tool for the definition of complex and stimuli-responsive 3D buckled shapes. Previous experimental methods, however, have focused on sheets that access a limited number of shapes pre-programmed into the sheet, restricting the degree of dynamic control. Here, we demonstrate on-demand reconfigurable buckling of poly(N-isopropylacrylamide-co-acrylic acid) (PNIPAM) hydrogel network films containing gold nanoparticles (AuNPs) by patterned photothermal deswelling. Predictable, easily controllable, and reversible transformations from a single flat gel sheet to numerous different three-dimensional forms are shown. Importantly, the response time is limited by poroelastic mass transport, rather than photochemical switching kinetics, enabling reconfiguration of shape on timescales of several seconds, with further increases in speed possible by reductions in film thickness.

Shape transformations driven by inhomogeneous in-plane distortion of thin membranes provide powerful routes to reconfigurable 3D materials. The incorporation of two or more independently addressable stimuli responsive materials or electronic heaters provides access to a larger number of pre-programmed shapes, but the difficulty of fabricating and controlling such patterned sheets increases rapidly with the number of orthogonally-controllable elements incorporated.

Light-addressable materials are of great interest in this respect, as they allow for continuous reprogramming into an arbitrary number of 3D shapes defined by patterns of illumination. While Kuksenok and Balazs have modeled gel sheets with light-controlled swelling based on the photoisomerization of spiropyran, this approach has not been experimentally realized. In addition, the reliance of photoisomerization-driven changes in swelling involves several drawbacks, most notably slow switching kinetics, incomplete reversibility, and the use of ultraviolet light. In contrast, photothermally-addressable hydrogels that rely on well-known volume-temperature transitions triggered by absorption of visible or infrared light offer switching speeds limited by mass transport, along with highly reversible and large changes in swelling. Given that the diffusion coefficient governing heat conduction is generally several orders of magnitude larger than that governing poroelastic mass transport, unsteady state temperature profiles generally do not provide a useful means for photothermally patterned buckling of hydrogel films. However, at steady state, well-defined spatially-varying temperature profiles can be established and used to pattern the swelling of gels.

Here, to achieve arbitrary and fully reprogrammable patterns of local deformation within a single hydrogel sheet, we take advantage of heat generated due to the surface plasmon resonance (SPR) absorption of ~4 nm diameter gold nanoparticles (AuNP), coupled with the thermal deswelling of poly(N-isopropylacrylamide-co-acrylic acid) (PNIPAM) hydrogels to drive patterned buckling of nanocomposite (NC) gel sheets, as illustrated in Figure 1A. The gels are prepared by radical polymerization of a monomer–AuNP mixture in water between two glass slides with defined spacing (details in experimental section). Small (nm-scale) squares are punched from the polymerized NC gel sheets and submersed in a phosphate buffer solution (pH = 7.3, 0.1 M NaCl) and illuminated with patterns of white light generated using a digital micro-mirror array, projected through an inverted microscope objective lens.

**Figure 1.** A) Schematic illustration and structures of photothermally reprogrammable gels. B) A single gel sheet is transformed from the flat state (i) subsequently into four selected shapes (ii–iv) defined by illumination with white light inside of the dotted boxes (iv: illuminated region is between the two squares).

Figure 1B shows selected fully reversible shape transformations of a single 25 μm thick NC gel sheet in aqueous solution at 30 °C (see also SV1). Regions illuminated with white light contract in volume, yielding steady-state buckled shapes that can be qualitatively understood from prior studies on sheets with pre-patterned deformation. A single rectangular stripe drives rolling into an axisymmetric “bottle-like” shape, stripes oriented at an angle to the sheet edges yields a helical...
roll (iii), illuminating the edges of the sheet yields a dome-like elliptic surface (iv), and illuminating one corner yields a wrinkled hyperbolic surface (v).

![Figure 2](image_url)

**Figure 2.** Temperature and intensity as a function of swelling ratio, d/d₀, where d₀ is the diameter at 22 °C without illumination. The inset shows the characteristic photothermal temperature increase as a function of intensity; the solid line shows a fit to the data at low intensities.

To better understand this light-induced deformation, we measure the linear swelling ratio (diameter d normalized by its initial value d₀ = 0.5 mm) of 100-µm-thick NC gel disks subjected to either flood illumination or global temperature changes (Figure 2). As expected, the gel shrinks in response to increases in both light intensity and temperature, and using the swelling ratio to map between the two curves yields a characteristic local temperature increase (∆T) provided by a given intensity (Figure 2, inset). Notably, ∆T increases nearly linearly with intensity until ∆T = 8 °C, at which point a break in the curve is seen, perhaps associated with the approach to the limiting de-swelling ratio of d/d₀ = 0.5, or the onset of convection (experimentally observed above ∆T = 5 °C). Based on these data, patterning experiments are carried out at 30 °C with light intensities of 5 W/cm², which allows for substantial changes in size with modest light intensities that minimize convection (corresponding to ∆T = 2 °C).

We next characterize the swelling kinetics using four gels with initial thicknesses h₀ from 25 – 100 µm, where the concentration of AuNP is adjusted to maintain equivalent absorbance of 0.15 (see SI). Each gel is first allowed to fully deswell under flood illumination at 22 °C, and subsequently re-swelled by turning the light off (Figure 3). Each data set is well-described by a single exponential curve, with time constants (Figure 3B, inset) that show a thickness dependence consistent with a poroelastic mass-transport limited process—that is, r ∼ h₀⁻¹. For sufficiently thin gels, this provides an important advantage over photochemical routes, in that the kinetics of swelling and deswelling can be finely tuned to desired speeds simply by altering the thickness or porosity of the gel. Here, we find characteristic response times of τ = 2 – 3 s for h₀ = 25 µm, while further increases in speed should be easily attainable using thinner gels.

![Figure 3](image_url)

**Figure 3.** A) Deswelling kinetics under flood illumination at 22 °C for gels with the indicated initial thicknesses (a control sample lacking AuNPs is shown for comparison), and B) subsequent re-swelling after the light is turned off. The inset shows a log-log plot of time constants (single exponential fits shown as solid lines in both A and B) versus thickness.

To exercise fine control over the photothermally-driven shape transformations of the NG gel sheets, we consider the steady-state temperature profiles generated under illumination. Neglecting convection, the temperature will be governed by Poisson's equation, i.e.

\[ \nabla^2 T = -\frac{q(r)}{k} , \]

where we treat the thermal conductivity k of the NC gel and water as equal. The volumetric heat generation rate q, is proportional to the product of the light intensity, and the absorbance by the gel at position r (where we ignore the gradient of light intensity through the thickness, appropriate for absorbance values well below 1). Thus, for any arbitrary pattern of light and configuration of the gel sheet, it is possible to solve for the resulting temperature profile using a Green's function method (see SI).

To provide a simple validation of this approach, we expose a square gel sheet to illumination within a rectangle of varying length l, causing the sheets to take on a rolled conformation, with greater curvature for larger l. The steady state greyscale intensity profiles along the midline are compared to the analytically calculated temperature profiles for a non-deformable sheet, mid-way through the gel thickness along the
corresponding line (Figure 4A). The measured widths of the deswelled regions (characterized by the full-width at half-maximum; FWHM) are slightly smaller than the expected temperature profiles (Figure 4B), most likely due to the reduction in the width of the region of heat generation caused by buckling. In addition to constant intensity illumination, smooth gradients of swelling of desired forms can be generated using halftoned patterns of illumination. For example, Figure 4B shows the configurations resulting from cubic, quadratic and linear gradients of light with equal integrated intensities (and thus heat generation). The deformation clearly becomes less localized as the projected intensity is distributed more broadly in space. Thus, while broadening of the projected patterns by thermal diffusion is intrinsic to the approach, by accounting for this broadening, the ultimate shapes of the gel sheets can be fine-tuned in a straightforward manner. More extensive de-swelling, and therefore more pronounced out-of-plane buckling can be achieved by reducing the crosslink density of the gel (see SV2); in this case, however, the extensive deformation of the sheet relative to its initial dimensions leads to less easily predicted changes in shape. Obtaining quantitative control of the full evolution of gel shape over time will require more detailed models that couple heat transfer with an appropriate poroelastic constitutive equation for the gel, allows for warping of the pattern of light as the gel deforms, and also considers factors such as the change in AuNP concentration with swelling, and the non-zero absorbance of light by the gel film.

Finally, we demonstrate directed motion by repeatedly sweeping a strip of light across a gel sheet, as seen in the supporting information (SV3). Interestingly, we find net motion in the direction of the sweep, whereas Kuksenok and Balazs observed motion in the reverse direction from simulations of photo-chemically patterned deformation.\(^{[13]}\) We speculate that perhaps the presence of time-varying temperature gradients are responsible for the opposite direction observed here, as Kuksenok and Balazs also found motion towards higher temperature regions under light sweeping with an orthogonal temperature gradient. While, fully understanding this difference requires further study, the ability to direct the motion of such gels in addition to dynamically reconfiguring their shape opens doors to highly adaptable elastic sheets.

In summary, we have developed a method to dynamically transform and reconfigure 2D hydrogel sheets into predictable and complex 3D shapes not limited by pre-programmed patterns within the material. Utilizing the SPR absorption of dispersed AuNPs and patterned illumination, localized photothermal deformation occurs in illuminated regions due to steady-state temperature gradients that can be understood by classical heat conduction equations. An almost limitless number of 3D shapes can easily be achieved from a single sheet. This demonstration paves the way for simple and on-demand tuneable soft robotics, drug delivery systems, and microfluidic devices.

**Experimental Section**

**Nanoparticle synthesis:** The synthesis of AuNPs has been described in detail elsewhere.\(^{[33]}\) Briefly, to an aqueous precipitate of tetrabutylammonium borate (Aldrich, 97%) was added to the vial, followed by heating using a pre-heated 55 °C oil bath, and finally, 0.087 g (10 eq.) of tert-butylamine borane (Aldrich, 97%) was added in one portion. The solution quickly turns from colorless to brown to light red-purple, and then darkens over the course of 2 h. The AuNPs were purified by three precipitation-centrifugation cycles – the solution was precipitated with 30 mL of THF, centrifuged (7800 RPM, 10 min.) and redissolved in 1 mL of methanol.

**Gel preparation:** To a Teflon lined vial containing 0.5 mg of dried AuNPs, 148 µL of a 0.24 g/mL aqueous solution of N-isopropylacrylamide (TCI, >98%), 30.5 µL of a 0.1 g/mL aqueous solution of sodium acrylate, 19.4 µL of a 0.02 g/mL aqueous solution of methylene bisacrylamide and 2.1 µL DI water, were added sequentially. The solution was degassed, and 1 µL of N,N,N,N'-tetramethyleneethylenediamicene (Aldrich, >99%) and 2 µL of ammonium persulfate solution (0.1 g/mL, Aldrich, >98%) were added to initiate polymerization. This pre-gel mixture was injected between two glass slides spaced by 100 µm Kapton spacers, placed in a vessel, purged with nitrogen and allowed to polymerize for ≥ 1 h. Gels were then placed in buffer solution and allowed to sit for ≥ 15 h, and then washed by two additional fresh buffer solution transfers. Squares and circles were manually punched from the gel sheets. Gels with thicknesses of 25, 50 and 75 µm were prepared using identical procedures, except with respective AuNP contents of 2, 1, and 0.67 mg.

**Microscope set-up:** All experiments were conducted using a Nikon Eclipse Ti inverted microscope with a Lumencore Spectra LED light source reflected off a Texas Instruments DLP Discovery 4100 digital micro-mirror array before reaching the objectives (4x, NA=0.2 & 10x, NA=0.5).

**Figure 4.** Fine tuning shape transformations of a single gel sheet. A) A light strip of increasing width (i, indicated by grey dotted lines, gives rise to increasing curvature of a 25 µm thick sheet; v. shows the calculated temperature profile (solid) and experimental intensity data (dots) with a dashed box indicating pattern size corresponding to image i; vi. compares the widths of the calculated temperature (dashed) and experimental greyscale profiles (solid). B) Smooth gradients in swelling with different functional forms are provided by halftoned patterns projected onto a sheet 50 µm in thickness.
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Patterns of white light are used to dynamically reconfigure photothermal nanocomposite hydrogel sheets into numerous 3D shapes. Fast and reversible transformations are achieved on time-scales tuneable down to several seconds. This concept for externally adaptable elastic sheets may find applications in soft robotics, drug delivery, or microfluidics.

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Photothermally-Reprogrammable Buckling of Nanocomposite Gel Sheets

Text for Table of Contents