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DNA-Engineered Hydrogels with Light-Adaptive Plasmonic Responses

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Orientational control of anisotropic plasmonic nanoparticles is an attractive proposition to generate dynamic plasmonic responses. Particularly, the use of light as a stimulus to modulate the orientation is extremely useful owing to its spatiotemporal operability. This work showcases a light-mediated approach to tune the orientational features of gold nanorods in DNA-engineered hydrogel materials. The strategy relies on the use of visible-light-induced photothermal effects to cause deformation of the hydrogel matrix, resulting in temperature-controlled polarization-dependent optical responses whose anisotropy features are highly adaptive to the nature of DNA crosslinks. The visible-light-mediated approach showcased here can open novel avenues to create dynamic light-responsive materials with reconfigurable plasmonic responses.

1. Introduction

The ability to sense and respond to environmental stimuli is a natural phenomenon found in most forms of life. In particular, appearance responses are universal, and they are often manifested as dynamic color modulation for camouflage and communication.[1–5] For instance, cephalopods can change their skin colors by regulating the orientation of chromatophores enclosed in an elastic sac, while also being able to macroscopically deform their body.[6–9] Such natural systems have inspired the fabrication of materials with emergent reconfigurable and adaptive optical properties, for example, soft actuating systems with camouflage abilities,[10,11] dynamic color displays,[12–14] and sensors for physiological and non-physiological conditions.[15–17]

Chromatophore analogues based on anisotropic plasmonic nanoparticles (ANPs) form excellent constituent elements for engineering biomimetic color features in materials. For example, ANPs such as gold nanorods (AuNRs) present two surface plasmon resonance peaks associated with longitudinal (LSPR) and transverse (TS) surface plasmon modes. Orientational control of AuNRs and selective excitation of their specific plasmonic modes can give rise to polarization-dependent dynamic colors.[18,19] There are multiple routes for controlling AuNRs orientation that have been investigated. Anisotropic plasmonic responses were achieved by incorporation of AuNRs into polymer matrices, where global orientational control and macroscopic coloration was obtained via stretching.[20–23] Polarization-dependent coloration was also realized under external magnetic fields where plasmonic nanostructures were modified by magnetic materials,[24–26] or by incorporation into liquid-crystal-based matrices where alignment of AuNR was modulated with electric fields.[27] Despite significant progress achieved in orientational control, considerable challenges remain. First, the external stimuli used for active orientational control must allow for programmable
modulation of optical properties beyond the need for just mechanical stretching. Second, anisotropic plasmonic nanostructures should be seamlessly integrated with the active media, that is, the process should not involve complex chemical functionalization and multiple phase transfer steps like in the case of liquid crystals[19,28,29] or include diverse wet chemical processes for modification with magnetic materials.[24,25]

DNA as a programmable nanoscale construction element has brought a transformative change in the ability to build, organize, and modify materials.[30–32] The inherent simplicity and predictability of Watson–Crick–Franklin base pairing, combined with responsiveness to ionic strength and temperature, makes DNA an excellent building block for programmable materials with adaptive responses.[33–35] For instance, in solution state, DNA-engineered fabrication strategies enabled coupled plasmonic structures with tailored optical properties offering control over spatial arrangement and stoichiometry, along with dynamic structural reconfigurability.[16–40] Whereas in solid state, DNA-tailored polymeric hydrogels have been used to achieve macroscopic shape transformations via swelling/de-swelling in response to external stimuli (pH, light, temperature, etc.)[41–45] However, the use of DNA-engineered optical elements for generating bulk color responses is still at infancy, and involves mostly the use of fluorophores.[46,47] DNA-engineered ANP responses have been demonstrated in solution but not widely explored in bulk macroscopic materials.[48,49]

To synergistically integrate DNA-functionalized ANPs into bulk materials, hydrogels constitute excellent enabling materials.[50–52] Hydrogels are crosslinked polymer networks with high water content (>90%) characterized by tunable structural and physicochemical parameters. These materials can easily be endowed with programmable triggers for implementing adaptive responses in tune with the surrounding environment. In this regard, the use of light as a stimulus to induce material transformations is particularly attractive owing to its remote control, customizable features (wavelength, intensity), and high spatiotemporal resolution. Light-responsive hydrogel systems are commonly fabricated through inclusion of photosensitive entities into hydrogel matrix[53–55] for reversible mechanical deformations either by photochemical or photothermal processes.[56–58] However, such efforts have largely been focused on inducing macroscopic shape transformations toward soft robotics[59–62] or photothermal-based therapeutic applications[63–66] rather than controlling orientation of ANPs and their plasmonic responses.

The concept of using photothermal effects to modulate the orientational features of ANPs in a hydrogel matrix is challenging for two reasons. First, the light-induced material transformations should not induce large changes in the mechanical properties which can potentially lead to randomized orientations of ANPs. Second, to translate the mechanical changes into optical outputs, the optical components, that is, gold nanorods should be integrated in the hydrogel matrix ideally with well-defined molecular linkers that can induce orientational changes upon the application of stimulus. However, such an integration is not easy in nanocomposite systems and often requires precise molecular engineering of the hydrogel matrix as well as the ANPs. These challenges, perhaps, explain why mechanical-based and LC-mediated approaches remain the most used methodologies to modulate orientation of ANPs and their plasmonic resonances.

Here, we present DNA-engineered hydrogel systems with light programmable polarization-dependent plasmonic responses. Our approach involves the use of DNA-functionalized gold nanorods with a deformable hydrogel matrix. To generate plasmonic hydrogel nanocomposites, we combine photopolymerizing monomers with hydrogen bonding ability, with DNA-functionalized gold nanorods as crosslinkers that function both as photothermal heat generators, and as chromatophore analogs. By utilizing a visible-light-mediated photothermal process to induce delinking of the hydrogen bonded hydrogel matrix and DNA duplexes, we achieve temperature-controlled reconfiguration of gold nanorod orientation. Importantly, we demonstrate fabrication procedures and molecular design that is simple and easily adaptable to other DNA-engineered plasmonic systems. This work opens avenues for achieving light programmable orientational control of anisotropic nanoparticles toward reconfigurable plasmonic responses.

2. Results and Discussion

2.1. Molecular Design and Components

The fundamental feature of the light-adaptive plasmonic responses in our systems relies on the molecular design of the hydrogel networks. The underlying design incorporates well-defined thermo-reversible hydrogen bonds that dissociate in response to light-induced photothermal effects. To this end, we designed a loosely crosslinked hydrogel matrix consisting of hydrogen bonding polymer networks of acrylamide (AM) and acrylic acid (AA). The acrylamide group is known to be a hydrogen bond acceptor, while acrylic acid is a hydrogen bond donor.[67,68] Photopolymerization of AM and AA leads to the formation of the polymer phase stabilized by hydrogen bonding interactions between amide and carboxylic acid groups. Furthermore, AuNRs functionalized with double-stranded DNA (dsDNA) were introduced as multi-valent crosslinkers (Figure 1).

AuNRs were synthesized following seed-mediated growth method with aromatic additives.[69] The average length and diameter of the rods were 65.5 ± 4.5 nm and 29.6 ± 3 nm respectively (Figure S1, Supporting Information). The LSPR and TSPR were located at 650 and 520 nm in solution, respectively (Figure S2, Supporting Information). In our system AuNRs act as both photothermal transducers and as plasmonic chromatophores.

To prepare AuNRs functionalized with temperature-responsive DNA duplexes (DNA-AuNR), we first attached thiolated single-stranded DNA strands as anchors. Then, complementary ssDNA linker strands bearing acrydite group were hybridized with the anchor strands at a suitable thermal annealing temperatures (Table S1, Supporting Information) (Figure 1A). Acrydite-functionalized DNA strands have been previously shown to covalently integrate with hydrogel networks.[142,70] Furthermore, to impart the hydrogel networks with programmable thermo-mechanical features, we hybridized three DNA duplexes (-SH anchor/acrydite linker) (Table S2,
Supporting Information) with varying lengths of linker and anchor strands. For DNA1-AuNR, the linker strand is 44 nucleotides (nt) long, and only its terminal part is hybridized with the 16T-thiol anchor strand, thus behaving like a flexible crosslinker. On the other hand, for DNA2-AuNR and DNA3-AuNR the linker strands are 14 and 30 nt long and turn fully as dsDNA after hybridization with the anchor strand, indicating the rigid nature of the crosslinkers. Furthermore, each DNA strand contained base pairing domains of increasing length 10, 14, and 30 base pairs. This confers them with varying degrees of melting temperatures of <20 °C (low), ≈45 °C (medium), and ≈82 °C (high), as determined by Nupack\[71\] (DNA concentration: 5 µM, Na⁺: 1 M). Successful functionalization of AuNRs with dsDNA was confirmed with agarose gel electrophoresis (Figure S3, Supporting Information). To quantify the DNA coverage, we utilized UV–visible spectroscopy-based quantification procedure for unlabeled DNA.\[72\] The extinction coefficients for individual anchor strands were calculated using Equation (S5), Supporting Information. The AuNRs were etched using KCN solution and the reaction was deemed completed when the AuNR solution became colorless (Figure S4, Supporting Information). From the quantitative estimates of DNA (Equation (S6), Supporting Information), although AuNRs were incubated with same concentration of thiol strands the coverage varied between the strands (Table S3, Supporting Information). The coverage is not only affected by the length of the linker strands, but also by the affinity of DNA bases to gold surface. In the case of DNA1-AuNR, the anchor strand is a 16 nt thiol strand containing thymine bases that has low affinity to gold.\[73–75\] Such a strand can be expected to be in an extended rod-like molecular configuration with a low coverage of DNA.\[76\] For DNA2-AuNR, the 14 nt thiol strand contains three adenine bases with high affinity to gold.\[74\] The high coverage of anchor DNA is in line with the observation that short DNA strands lead to high coverage with an extended conformation.\[76\] Finally, with respect to DNA3-AuNR, the 30 nt thiol strand is expected to have an extended conformation, however, the entropic costs associated with long strands can result in lower coverage.\[76\] The corresponding footprint calculations (Equation (S7), Supporting Information) indicate that coverage was well below the estimates for a dense monolayer coverage.

Subsequently, hydrogel films were prepared by photopolymerization of the individual components under UV irradiation at 365 nm (Figure 1B). In a one-pot approach, the pre-gel solutions consisting of acrylic monomers (both amide and acid) combined with DNA-AuNR, a small amount of α-ketoglutaric acid (photo-initiator), and bis-acrylamide was photopolymerized to achieve the formation of a stable hydrogel film (concentrations
of the individual components are given in Table S4, Supporting Information). A key feature of our hydrogel design lies in the utilization of high monomer concentration and low crosslinker content to achieve the formation of hydrogel network with viscoelastic features (Figure 1C,D). Such a strategy has been previously used to obtain tough and stretchable hydrogels, attributed to the presence of large amount of physical entanglements, causing efficient energy dissipation of polymer chains under the application of mechanical and light stimuli. The combination of high acrylic monomers concentration and low amount of DNA-AuNR crosslinks can result in the formation of physically entangled hydrogel network with deformable crosslinks. Such a hydrogel network structure is expected to undergo local, transient, photothermal-mediated programmable deformations leading to tunable orientation of AuNRs.

2.2. Thermo-Mechanical Characterization

To quantitatively characterize the mechanical properties of the hydrogel networks with three different DNA duplexes in DNA-AuNRs, we performed magnetic-bead-based microrheology experiments at room temperature. For the microrheological characterization, magnetic and non-magnetic beads were incorporated into the hydrogel networks. Then, particle movements were maneuvered using controlled forces applied by a magnetic micromanipulator. The subsequent displacements of the magnetic beads were tracked with respect to non-magnetic beads using an optical microscope. The tracked displacements were fitted to obtain the amplitude and the phase angle of magnetic-bead motion that allow for the calculation of complex shear modulus ($G^*$) and loss tangent ($\tan \delta$) of the hydrogel networks. The thermo-responsive features of the hydrogel networks were investigated using dynamic mechanic analysis (DMA). As shown in Figure 2C, temperature sweeps in DMA, for example, indicate that at room temperature crosslinked gels are less viscous in nature.

Focusing on the DNA-AuNR crosslinked gels, the $G^*$ values for gels with duplexes (1-3) are found to be 2565.20 ± 673.60, 1275.90 ± 272.20, and 1784.50 ± 567.40 Pa, compared to control gel 744.70 ± 473 Pa. The higher $G^*$ values with DNA-AuNR crosslinks indicate the dominating contribution of DNA-AuNR toward enhancing the elastic component of the gels. The difference in $G^*$ values between DNA duplexes is likely due to the varying coverage of AuNRs by the thiol-modified anchor strand (Table S2, Supporting Information) and the molecular conformation of the linker strand which affects the binding with the anchor strand, thereby influencing the crosslinking to the hydrogel networks. For example, the flexibility of DNA1-AuNR crosslinker results in stronger shear modulus values despite lower coverage of anchor strands compared to gels crosslinked with rigid crosslinkers. This is in line with previous observation that flexible crosslinkers and low crosslinking content can result in homogenous hydrogel network resulting in tough hydrogels. In addition, the DNA crosslinked gels exhibited lower loss tangent values when compared to the control gel, indicating that at room temperature crosslinked gels are less viscous in nature.

The hydrogels exhibited both linear and nonlinear hydrogel stress–strain relationships analogous to viscoelastic materials owing to the presence of both chemical and physical crosslinks (Figure 2B and inset). The combination of high monomer content, involving hydrogen bonded association between the AM and AA groups, and the DNA-AuNR crosslinks confers them with extraordinary stretchable features with elongation break at over 1000% tensile strains. In contrast, the control gel without DNA-AuNR exhibited elongation break at 900%. However, gels crosslinked with flexible crosslinker of DNA1-AuNR exhibit higher tensile properties compared to gels crosslinked with rigid crosslinkers of DNA (2-3)-AuNR. Such an observation suggests that flexible crosslinkers, compared to rigid crosslinkers, provide strong crosslinking features between the polymer chains, as seen previously by Wei et al.

The thermo-responsive features of the hydrogel networks were investigated using dynamic mechanic analysis (DMA). As shown in Figure 2C, temperature sweeps in DMA, for example,
DNA1-AuNR crosslinked hydrogel network exhibited a clear thermal transition ($T_T$) located at ≈57 °C, where the material behavior changes from a high to low stiffness state (loss modulus > storage modulus) with a dramatic loss in storage modulus from 9.5 to 2.0 kPa (about 80%) in the temperature range between 30 and 70 °C. Such a drastic loss can be attributed to complete dissociation of the DNA duplexes along with the dissociation of hydrogen bonds between polymerized AM and AA. For DNA2-AuNR crosslinked gels, the transition temperature ($T_T$) was located at ≈38 °C and the storage modulus reduced from 6.7 to 4.3 kPa (about 36%). With respect to DNA3-AuNR, the transition temperature ($T_T$) was located at ≈52 °C and with the hydrogel undergoing reduction in stiffness from 9.2 to 7.2 kPa (about 22%) (Figure S5A,B, Supporting Information). The smaller reduction in storage modulus values for DNA (2,3)-AuNR when compared to DNA1-AuNR can be attributed to the higher melting temperatures of the rigid duplexes. By contrast, in the control gels the storage modulus changed from 17.7 to 13.4 kPa (∼24%) in the temperature range 30–70 °C likely due to the thermal dissociation of hydrogen bonds between acrylamide and acrylic acid groups (Figure S5C, Supporting Information). A broad peak in loss factor (tan $\delta$) appears at ≈75 °C, corresponding to the glass transition ($T_g$) in both crosslinked and control gels. The change in mechanical properties corresponding to the dissociation of the hydrogen bonding interactions between AM and AA groups in tandem with thermal melting of the DNA duplexes, forms the basis for the molecular design strategy of photothermal tuning of plasmonic responses.

2.3. Mechanical Tuning of Plasmonic Responses

The stretchability features of the hydrogel nanocomposites led to the investigation of orientational control of gold nanorods by mechanical strains. It is well known that the alignment of anisotropic nanoparticles along the stretch direction can generate polarization-dependent optical responses.[20,23,86,87]

To investigate the polarization-dependent optical responses of the hydrogels, the films were stretched at varying strains from 0–500% (Figure 3A). A homemade set-up was designed

![Figure 3](https://example.com/figure3.png)

**Figure 3.** A) Schematic illustration indicating the polarization and the propagation direction of light with respect to the stretching direction. B) DNA2-AuNR crosslinked hydrogels absorption spectra under varying strain (0–500%) for DNA2-AuNR crosslinked hydrogels with light polarization perpendicular to the stretching direction. C) DNA2-AuNR crosslinked hydrogels absorption spectra under varying strain (0–500%) for DNA2-AuNR crosslinked hydrogels with light polarization parallel to the stretching direction. The spectra were normalized at 450 nm. D) Tensile strain dependence of anisotropic optical responses evaluated by quantifying dichroic ratio at 660 nm. The data is represented as mean ± standard deviation for three independent measurements (n = 3) for each sample. E) Photographs of the composites at 500% strain taken under linearly polarized light illumination perpendicular and parallel to the stretching direction. Scale bar: 1 cm.
to measure the optical responses. Briefly, a linear polarizer was placed between the hydrogel film and the light source (Figure S6A,B, Supporting Information). The hydrogel film was attached either stretched or unstretched to a circular aperture plate. To compare the polarized optical spectra in both parallel and perpendicular directions with respect to the direction of light, the data was normalized at 450 nm. As shown in Figure 3B, the normalized data for gels crosslinked with DNA2-AuNR, when the incident light was polarized perpendicular to the stretching direction the amplitude of LSPR at 660 nm gradually reduced with increasing strain, while amplitude of TSPR remained the same. The LSPR mode of AuNRs was intensively excited when the incident light was polarized parallel to the stretching direction (Figure 3C). This indicates a significant anisotropic light absorption originating from AuNRs alignment caused by stretching. Similarly, for gels crosslinked with DNA1-AuNR and DNA3-AuNR the LSPR peak at 660 nm was intensively excited under parallel polarized light, with a little change in the TSPR peak in both parallel and perpendicular polarized perpendicular excitation (Figure S6, Supporting Information). Furthermore, the anisotropic alignment features were quantified by calculating the dichroic ratio (DR) (Equation (S4), Supporting Information) at varying tensile strains (DNA(1-3)-AuNR) at LSPR 660 nm (Figure 3C). DR is a useful parameter to quantify the degree of alignment of nanorods and thereby the polarized optical responses can be understood. For all the gel systems investigated here, the DR increased with increasing tensile strains. Since the AuNRs are crosslinked to the polymer network, the variation in the dichroic ratios among the duplexes is a result of varying nature of the crosslinks. For example, DNA2-AuNR exhibited the highest dichroic ratios among the examined systems. This can be correlated to the presence of most number of anchor strands (Table S3, Supporting Information), that may allow establishing enough acrylate-modified linkers facilitating more anchoring to the hydrogel matrix. While the stiffer nature of DNA3-AuNR result in lower dichroic ratios. When the hydrogel films were sufficiently stretched (≥400%) the anisotropic responses saturated.

To confirm the feature of higher AuNRs alignments in hydrogel with DNA2-AuNR crosslinks, photographs were taken under incident light linearly polarized in directions parallel and perpendicular to the stretching (for set up, see Figure S6C, Supporting Information). As seen in Figure 3E, the films showed strong green and red colors highlighting the selective excitation of the longitudinal and transverse peaks. In contrast, for gels crosslinked with DNA1-AuNR the color responses were rather weak, for DNA3-AuNR no noticeable colors were found both in parallel and perpendicular light excitation, confirming our observation that DNA crosslinks restrict reorientation of AuNRs.

2.4. Light-Mediated Plasmonic Tuning

To investigate the light-adaptive plasmonic properties of the hydrogels we utilized photothermal features of AuNRs. The photothermal energy was used to remotely trigger delinking of the hydrogen bonded networks of the hydrogel films.

A red-light LED with an emission maximum of 660 nm was chosen as the light source, which is matching with the LSPR of the AuNRs in the hydrogel matrix. The concentration of AuNRs was kept constant at 3 nm for all the AuNR-DNA crosslinked networks as well as the sample without DNA crosslinks. The photothermal properties of the hydrogel films were quantified using an infrared camera facing the sample in the forward direction. The spatiotemporal evolution of the heat maps was captured at light intensities of 0.67, 1.33, and 1.67 W cm⁻² by keeping the beam spread constant (≈2 cm) and covering the sample in its entirety barring the edges (Figure S8, Supporting Information). Upon light irradiation for 60 min, the heating curves followed an asymptotic behavior and reached maximum temperatures (Tmax) of 32, 48, and 70 °C based on the respective intensities (Figure SBD, Supporting Information). Furthermore, the cross-sectional heat profiles showed that spatial localization of the heat distribution was confined to the beam diameter (Figures S9 and S10, Supporting Information).

Initially, the light-adaptive plasmonic features were examined for DNA3-AuNR. The hydrogel films were stretched at 100% strain. The light-adaptive changes were evaluated at a light intensity of 1.67 W cm⁻² and irradiation duration of 20, 40, 60, 90, and 120 min. DR was utilized to evaluate the alignment features of AuNR. In the absence of light, the DNA3-AuNR crosslinked film was largely isotropic with a DR of 0.06 ± 0.02 (Figure 3A). The intensity of both TSPR and LSPR were slightly reduced in both perpendicular and parallel light excitation, owing to reduction in thickness of the film under the application of strain (Figure 4A). Upon light irradiation, when the temperature reached close to the thermal transition temperature (Tc) ≈52 °C of DNA3-AuNR (Figure 2A), the polarized optical spectrum displayed differential absorption in parallel and perpendicular directions, with enhanced absorption features. In this state, the hydrogel films exhibited an increase in anisotropy with a DR of 0.11 ± 0.02, revealing that hydrogel plasmonic properties adapted to the light intensity and the temperature (Figure 4B). Furthermore, when the temperature reached ≈70 °C, the longitudinal peak at 660 nm of AuNR was strongly excited and red-shifted to ≈700 nm, accompanied by increase in absorption features under both parallel and perpendicular light excitation. (Figure 4B). The hydrogel film in this state exhibited strong polarization-dependent optical behavior (DR = 0.21 ± 0.02) with a 282% increase in the DR when compared to the initial stretched state at 100% strain. In fact, the irradiated sample exhibited an enhanced degree of anisotropy when compared to the sample stretched at 500% strain (Figure 3D). Also, as the crosslinked AuNRs were strongly coupled to the polymer network, despite the intense irradiation, when the films were placed in a humidity chamber (64–68% relative humidity) over 90% optical properties were recovered (Figure 4C). When these films were further subjected to longer irradiation time (120 min) further increase in DR was achieved, however the humidity-induced recovery was partial (Figure S11, Supporting Information). Photographs of the DNA3-AuNR hydrogel films under linearly polarized light illumination at different time points were taken to qualitatively understand the evolution of colors after cooling the samples to room temperature. As seen in the images, films in the initial nonirradiated state did not exhibit any polarization-dependent coloration. However, upon light irradiation, the development of strong polarization-dependent colors can be clearly noticed (Figure 4D–F).
The dramatic change in plasmonic properties can be related to two events caused by material changes mediated by photothermal effects. First, the red-shift in the longitudinal peak position (Figure 4B) is related to change in refractive index in the surrounding media mediated by the photothermal heat-induced de-swelling of the composite matrix.\[^{[88]}\] This can further lead to enhanced absorption features due to increase in concentration of the AuNRs due to heat-induced reduction in the area of the composite film. Representative photographs of hydrogel films at various stages of stretching, irradiation, and recovery can be found in Figure S12, Supporting Information. Second, since the nanorods are well dispersed and crosslinked to the hydrogel matrix, each nanorod essentially acts as a local heating element that effectively transduces light into heat. The photothermally induced temperature increase leads to the change in the elastic modulus of the hydrogel networks, including melting of DNA-AuNR crosslinks (Figure S13, Supporting Information). In such a state, the hydrogel phase surrounding the AuNRs can behave as fluid\[^{[89]}\] allowing dynamic reconfiguration of AuNR orientation, and leading to the increased anisotropy in AuNRs orientation.

Next, the light-adaptive plasmonic features of polymer networks crosslinked with DNA1-AuNR were examined (Figure 5A). The film in a stretched state at 100% strain with no light irradiation exhibited a DR of 0.1. When the light irradiation was switched on, and the temperature reached $\approx 32^\circ\text{C}$ the dichroic ratio improved from 0.1 ± 0.04 to 0.18 ± 0.05. However, at higher intensities of light irradiation, that is, 1.33 and 1.67 W cm$^{-2}$, the dichroic ratios largely remained constant. Amongst the duplexes studied, DNA1-AuNR undergoes the largest change in the modulus between 30 and 70 °C (Figure 2C). Such a large change in modulus afforded complete humidity-mediated recovery of alignments but did not lead to dramatic improvement in the orientation of AuNRs (Figure S14C, Supporting Information).

Figure 4. Polarized absorption spectra of DNA3-AuNR stretched at 100% strain at various adaptive stages. A) Before irradiation. B) At 50 and 70 °C. C) Overnight recovered sample. D–F) Evolution of polarized adaptive color responses of DNA3-AuNR crosslinked hydrogels with incident light polarized perpendicular and parallel to stretching (100%). Representative sample ($n = 1$) Scale bar: 1 cm.

Figure 5. Evolution of adaptive plasmonic properties with temperature for DNA(1-3)-AuNR hydrogels stretched at 100% strain. The data is represented as mean ± standard deviation for three independent measurements ($n = 3$) for each type of sample.
In the case of DNA2-AuNR, the film in a stretched state (100%) is anisotropic (DR = 0.30 ± 0.09) with a weak polarized optical response as seen in Figure S15, Supporting Information. Upon light irradiation, when the temperature reached the transition temperature of 38 °C, anisotropic absorption features improved with a DR of 0.44 ± 0.03 (Figure 5A). Further increase in temperature to 48 °C led to stronger polarized optical responses with a DR of 0.48 ± 0.04. When the temperature was at 70 °C, DR does not improve but declines to 0.35 ± 0.03 (Figure 5A), likely due to the higher degree of hydrogel deformation. The humidity-mediated recovery leads to over 90% recovery of optical properties (Figure S15C, Supporting Information). To further confirm the DNA2-AuNR alignment, cryo-TEM images were acquired from hydrogel samples at various stages. In unstretched samples AuNRs were randomly oriented (Figure S16, Supporting Information), while the irradiated samples at a 100% strain were oriented along the direction of stretching (Figure S17, Supporting Information). With respect to humidity-mediated recovered samples, the cryo-TEM images (Figure S18, Supporting Information) indicated random alignment of AuNRs. Next, we investigated the reversibility and repeatability of the photothermal-mediated process. DNA (1-3)-AuNRs crosslinked gels were exposed to light irradiation at 1.67 W cm⁻² intensity over five cycles (Figure S19, Supporting Information). The polarizable optical features were recoverable with DNA1-AuNRs exhibiting complete recovery of optical properties after each cycle, in line with previous observation (Figure S14, Supporting Information). With respect to DNA (2-3)-AuNRs the optical properties were stable, however the degree of recovery varied between each cycle (Figure S19 B,C, Supporting Information).

Furthermore, when the samples were stretched at 500% strain and subjected to light irradiation for 40 min at 1.67 W cm⁻² the DNA1-AuNR crosslinked hydrogel underwent complete depolarization, in which anisotropic absorption features were significantly reduced (Figure S20A, Supporting Information) with DR decreasing from 0.38 to 0.07. With respect to DNA2-AuNR the anisotropic optical features reduced with dichroic ratio decreasing from 0.4 to 0.2 (Figure S20B, Supporting Information). The light-induced temperature changes can not only be used to enhance polarization features, but also to induce depolarization of the films. Such a change is possible due to programmable mechanical deformations linked to optical outputs mediated by DNA-AuNR crosslinks. On the contrary, the anisotropic absorption DNA3-AuNR crosslinked hydrogels stretch at 500% was enhanced with DR improving from 0.14 to 0.30. Interestingly, such an enhancement resembles light-mediated alignments obtained in a stretched state at a 100% strain (Figure S20C, Supporting Information).

Finally, to evaluate if DNA crosslinks are essential for light-mediated orientational control, we fabricated a hydrogel film where AuNRs were not linked to the polymer network. Upon exposure to light irradiation of the highest intensity (1.6 W cm⁻²), the longitudinal peak at 660 nm of AuNR was intensively excited accompanied by increase in absorption features under both parallel and perpendicular directions to the incident light. However, such an increase did not improve the initial AuNRs alignment, that is, the dichroic ratio did not improve beyond the initial value of 0.6 (Figures S21 and S22, Supporting Information). This indicates that photothermal heating only led to the shrinking of the hydrogel matrix but did not improve the orientational features of the gold nanorods. In addition, upon placing the samples in a humidity chamber the recovered samples remained largely anisotropic. Therefore, the DNA crosslinks not only provide adaptable features to the hydrogel network but also serve as a memory element, aiding in the recovery of optical properties.

It is important to highlight the concept of photothermal energy cascades engineered in our system. As demonstrated previously,[90,91] light-mediated energy cascades can result in materials whose properties are adaptable to the light intensity. In our case, we demonstrate the use of visible-light-mediated photothermal energy cascades to achieve programmed mechanical deformations, to gain reconfigurable and temporal control over gold nanorod orientation in hydrogels. The temperature-mediated evolution of macroscopic color responses obtained here are similar to dynamic appearance changes displayed by vetebrate species for their survival.[92,93] While mechanical adaptability was demonstrated in the current work is in line with previous studies.[20,21,94] Stretching-mediated modulation of AuNRs alignment invariably leads to decrease in AuNRs concentration, owing to reduction in thickness of the film, which in turn may lead to weak macroscopic colors. Such approaches required relatively high concentration of about 0.2–1 wt% of AuNR with respect to polymer content.[21,94] Whereas our photothermal-mediated approach eliminates the need for high concentration of AuNRs besides providing dynamic modulation and recovery of polarizable optical features. Furthermore, previous works on light-mediated alignments of anisotropic nanostructures either involved the use of liquid crystal molecules that are intrinsically anisotropic or thin polymer films in the range of 8–30 µm[95–98] and included the use of specialized laser-based light sources. Given that our samples are bulk hydrogel composites and involve the use of a simple visible-light LED, the photomodulation we achieved here is quite remarkable.

3. Conclusions

In summary, we demonstrated a visible-light-mediated photothermal approach to showcase adaptive plasmonic properties in hydrogel composites. This was facilitated by DNA-engineered viscoelastic hydrogel networks that can undergo programmable light-mediated deformations. The light-induced temperature responses led to structural changes in the hydrogel films, leading to polarized optical responses that were adaptive to the nature of DNA crosslinks and light intensity. The significant feature of this study includes the first demonstration of photothermal modulation of orientational features of gold nanorods to realize strong polarization-dependent macroscopic colors. While polarization-dependent optical responses of DNA-engineered nanoparticle systems have been demonstrated in solution, translating such features to bulk is challenging. Our molecular design coupled with synergistic integration with hydrogel materials presented here is simple and can be easily adapted to other DNA-engineered plasmonic systems. This can further lead to advancement of reconfigurable plasmonic systems with tailored optical responses.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

S.M. and J.R. conceived, designed, and performed the experiments. A.K. supervised the study. M.-K.N. synthesized the AuNRs. A.J.L. and J.P. carried out the micromechanical characterizations. J.L. designed the polarized optical measurement setup and obtained polarized optical photographs of the gels. J.S. performed the cryo-TEM microscopy experiments. Y.H. assisted with AuNR-DNA functionalization. B.N.N. contributed toward optimization of the hydrogel synthesis procedures. J.R., S.M., and A.K. wrote the manuscript with contributions from all the authors.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

active plasmonics, DNA, hydrogels, light responsiveness, photoalignment

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