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Rapid photothermal actuation of light-addressable, arrayed hydrogel columns in a macroporous silicon membrane

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Abstract

This paper presents rapid photothermal actuation of light-addressable, arrayed hydrogel columns in a macroporous silicon membrane. Au nanorods are incorporated into thermo-responsive p-NIPAAm hydrogel to utilize surface plasmon-induced local heating by near-infrared light. By measuring optical transmission through the fabricated membrane structure with Au nanorod embedded hydrogel, we have demonstrated that photothermal actuation of hydrogel can be done in two-dimensional, pixel-like configuration with high spatial and temporal resolutions. Benefiting from the hydrogel volume confinement within micron-sized pores, we have achieved sub-second response time of hydrogel photothermal actuation and its repeatable photothermal actuation on highly localized illuminated area. Considering that each hydrogel column is confined within each pore and different wavelength of light can be used to induce photothermal actuation of hydrogel's deswelling characteristics by modifying physical dimensions of Au nanorods, it has a potential for optically-addressable, multiplexed drug release systems with rapid response time.

Graphical Abstract

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Keywords

thermo responsive hydrogel; photothermal; macroporous silicon membrane; Au nanorods

1. Introduction

Stimuli responsive hydrogels are considered as smart materials because it undergo reversible phase transition by external stimuli and return to initial phase when the stimuli are removed. Reversible phase transition of hydrogels at cloud point in optical(transparent/opaque), physical(swelling/de-swelling) and chemical(hydrophilic/hydrophobic) properties can be utilized in various applications actuated by external stimuli such as light, temperature, pH, gas, ion, electric and magnetic fields [1, 2]. Among the stimuli responsive hydrogels, thermo responsive hydrogels are of great interest in biomedical applications such as smart switches and actuators [3–5], drug release [6], diagnostic [7], sensors [8], and tissue engineering [9]. Especially N-isopropylacrylamide (NIPAAm) based thermo responsive hydrogel has been extensively investigated because it exhibits reversible phase transition at its lower critical solution temperature (LCST) near human body temperature, and the LCST is readily controlled by copolymerizing with propylacrylic acid(PAA) based monomers [10].

Phase transition of thermo responsive p-NIPAAm hydrogel have been demonstrated using various temperature stimulus methods depending on the phase changing area/volume such as ambient medium [11, 12], micro heater [13], and nanostructures [14–16]. Light assisted phase transition of thermo responsive hydrogels enables locally- controllable non-contact applications via light absorbing materials including metallic nanostructures, carbon nanomaterials, organic polymer materials, and organic dyes [17, 18]. Especially, light absorbing materials responding to near infrared (NIR) band are of great interest in bio medical applications since NIR can penetrate body tissues with minimal absorption. Among

light absorbing materials responding in NIR band, gold (Au) nanorod has been popular and safe choice for light assisted biomedical applications because it shows high photothermal conversion efficiency, tunable surface plasmon resonance (SPR) behavior, and biocompatibility [19–22].

Incorporation of Au nanorods into this thermo-responsive hydrogels opens new class of applications such as light actuated structures [23]. For example, Sutton *et al.* demonstrated a new type of active cell culture platform that can be reversibly deformed [24], Zhang *et al.* presented photo-controlled electrical/mechanical switch based on the Au nanorod/p-NIPAAm fiber composite especially suitable under acidic or basic conditions [14], and Zhang *et al.* demonstrated heat and anti-cancer drug delivery using Au nanorods encapsulated hydrogel [7].

In this paper, we demonstrate photothermal actuation of Au nanorod embedded p-NIPAAm hydrogel columns in a macroporous silicon membrane by near-infrared (NIR) light. Micron-sized arrayed hydrogel columns incorporated with Au nanorods are precisely formed within predefined pores in a macroporous silicon membrane, which physically separates each hydrogel column. By forming the micron-scale hydrogel columns within pores, we have achieved sub-second, reversible photothermal actuation of the hydrogel columns. Furthermore, individual pores can be viewed as three-dimensional, vertical microfluidic channels containing light-actuated hydrogels considering their dimension. This can be significantly different from the conventional two-dimensional microfluidic configurations with hydrogels [25–28] by utilizing new perspectives of high-density fluidic channels. We have shown that two-dimensional, pixel-like, arrayed hydrogel columns can be locally and rapidly controlled by light. This may allow novel light-directed drug release systems based on unique deswelling property of the thermo responsive hydrogel. Such systems can benefit applications in the area of chemical stimulations of neuronal networks [29–32] that require high spatiotemporal resolution of drug release.

2. Design and Fabrication

2.1 Design

A schematic structure of Au nanorod embedded p-NIPAAm hydrogel columns in a macroporous membrane is illustrated in Fig. 1(a). In the demonstrated structure, an array of micron-sized through-pores are periodically arranged in a macroporous silicon membrane to form pixel-like, two-dimensional hydrogel columns. Au nanorods with specific absorption band are incorporated in p-NIPAAm hydrogel and the resulting hydrogel composite infills the pores to form arrayed hydrogel columns. At the temperature below the LCST of the hydrogel, light can be transmitted to the other end of the macroporous membrane via transparent p-NIPAAm hydrogel columns as waveguides. As the temperature of the hydrogel columns in/near the surface of the macroporous silicon membrane is raised over the LCST by external stimuli, the transparency of p-NIPAAm hydrogel changes to opaque and light transmission is blocked as shown in Fig. 1(b). Simultaneously, the hydrogel columns are deswelled and release liquid in hydrogel columns through micron-sized pores. In the proposed design, the external stimulus is NIR light, which is corresponding to the SPR absorption band of incorporated Au nanorods.

2.2 Materials

N-isopropylacrylamide (NIPAAm) and Silver Nitrate (AgNO_3) were purchased from TGI America. N,N'-Methylene-bis-acrylamide (MBAAm), ammonium persulfate (APS), ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), N,N,N',N'-tetramethylethylenediamine (TEMED), and Polyvinylpyrrolidone (PVP) were purchased from VWR. Chloroauric acid (HAuCl_4), Sodium borohydride (NaBH_4), and Hexadecyltrimethylammonium bromide (CTAB) were purchased from Sigma Aldrich. They were used as received without further purification. Deionized (DI) water (Reagent Grade, Electron Microscopy Sciences, Inc.) was used for all solutions.

2.3 Synthesis of Gold nanorods

Gold (Au) nanorods were synthesized by seed mediated synthesis method [20, 33]. First, for Au seed preparation, 0.25 mL 10 mM HAuCl_4 was diluted with 9.75 mL 0.1 M CTAB and stirred with a magnetic stirrer at 1000 rpm. While vigorously stirring the mixture of CTAB and HAuCl_4 , ice-cold 600 μL 10 mM NaBH_4 was quickly injected to the mixture. After 10 minutes of vigorous stirring, the solution was aged for 2 hours without stirring. The temperature during Au seed synthesis was maintained at 25°C . Second, for Au nanorod synthesis, 50 – 150 μL 10 mM AgNO_3 was added to 9.5 mL 0.1M CTAB solution, followed by addition of 500 μL 10 mM HAuCl_4 and 55 μL 0.1M ascorbic acid. Once the color of the solution became clear after gentle agitation, freshly prepared 12 μL Au seed solution was added and left for 2 hours at 27°C . To prevent further growth of Au nanorods, a pellet of Au nanorod precipitate was obtained from freshly synthesized Au nanorods suspension by centrifugation at 9000 rpm for 40 minutes. The expected dimensions of Au nanorods are about 47 nm in length, about 12 nm in diameter and about 4.5 in the aspect ratio [34].

2.4 Thermo-responsive p-NIPAAm Hydrogel preparation/polymerization

For obtaining about 1 cm^3 thermo-responsive p-NIPAAm hydrogel, 0.1 g of NIPAAm monomer and 0.002 g of MBAAm crosslinker were dissolved in 1 mL DI water followed by bubbling with nitrogen for 30 minutes to degas oxygen in solution. After degassing of oxygen, 20 μL of 5 wt % APS initiator and 1 μL TEMED accelerator were added for polymerization in nitrogen ambient.

2.5 Macroporous silicon membrane preparation

Periodically arranged, one-side opened 500 μm thick macroporous silicon was purchased from Smart Membranes, Germany. To make through-hole macroporous silicon membrane, the back-side of silicon was lapped using a lapping machine (Buehler Minimet). First, macroporous silicon was mounted using wax on a lapping mount and lapped using slurry solution containing 1 μm alumina powders until pores were visible from the bottom of the macroporous silicon. Additional back-side polishing was performed using slurry with 0.25 μm alumina powders to obtain smoother surface. Since pore diameter affects light transmission characteristics [35], the pores were enlarged by repeated thermal-oxidation and buffered oxide etching processes. The resulting macroporous silicon membrane has 500 nm thick silicon dioxide layer along the pore walls.

2.6 Photothermo p-NIPAAm hydrogel in macroporous silicon membrane

It is critical to disperse Au nanorods uniformly in water-based p-NIPAAm hydrogel solution in order to obtain reliable photothermo effect from Au nanorods embedded p-NIPAAm hydrogel via surface plasmon resonance. As-synthesized Au nanorods are terminated with CTAB, which makes positively charged Au nanorods. When CTAB terminated Au nanorods are dispersed in water (effective dipole moment 2.4 debye) based p-NIPAAm solution, Au nanorods aggregate and result in non-uniform dispersion in the p-NIPAAm hydrogel. In order to obtain uniformly dispersed Au nanorods in water-based p-NIPAAm solution, positively charged CTAB termination must be capped by a surfactant, which leads slightly negatively charged Au nanorods. Au nanorods precipitate obtained from 20mL of as-synthesized Au nanorod suspension by centrifugation was re-suspended in 2 wt. % PVP solution for 24 hours to convert to negatively charged Au nanorods. Again, PVP functionalized Au nanorods as a pellet was collected by centrifugation at 9000 rpm for 40 minutes.

Pellet of PVP capped Au nanorods was re-suspended in the mixture of 0.5 mL p-NIPAAm, and MBAAm mixture by ultrasonication followed by addition of 10 μ L 5 wt % APS and 0.5 μ L TEMED for polymerization.

Before filling with Au nanorods incorporated p-NIPAAm hydrogel solution in pores, the macroporous silicon membrane was treated with Piranha solution, a 3:1 mixture of concentrated sulfuric acid (H_2SO_4) with hydrogen peroxide (H_2O_2) for 10 minutes to make the surface of pore walls hydrophilic for increased wettability. After rinsing with DI water, the Piranha solution treated macroporous silicon membrane was immersed into the prepared p-NIPAAm, MBAAm APS, and TEMED mixture in a vial and ultrasonicated for 30 seconds to remove trapped air in pores. After the mixture was polymerized, unnecessary hydrogel over the membrane on one side was removed by a razor blade.

3. Result and discussion

3.1 Thermo-optical characteristic of p-NIPAAm hydrogel

A glass capillary tube (Outer diameter: 2.5 mm, inner diameter: 1 mm) is filled with pure p-NIPAAm hydrogel solution and polymerized. Image of Fig. 2(a) shows transparent p-NIPAAm hydrogel in a glass capillary tube at 18 °C and image of Fig. 2(b) shows milky p-NIPAAm hydrogel in a glass capillary tube at 40 °C. Thermo-optical characteristic of p-NIPAAm hydrogel is investigated by custom built Thermo-optical transmittance measurement setup as shown in Fig. 2(c). To investigate the optical transmittance of p-NIPAAm hydrogel as a function of temperature, pure p-NIPAAm hydrogel filled glass capillary tube was inserted in the 3 mm hole of an aluminum heating block of which the temperature is controlled by a temperature controller, and 635 nm visible laser light via multicore optical fiber was illuminated through a pinhole. The intensity of transmitted light through a p-NIPAAm hydrogel was measured with a photodetector using Keithley 237 High Voltage Source Measure Unit. Fig. 2(d) shows optical transmittance characteristic of pure p-NIPAAm hydrogel in the capillary tube as a function of temperature. The optical transmission characteristic clearly shows two distinct states with sharp transition of p-

NIPAAm hydrogel around 34°C. The thermo-optical characteristic of p-NIPAAm hydrogel shows typical hysteresis behavior of thermo responsive hydrogels.

3.2 Optical Characteristic of Au nanorods

The absorbance characteristics of Au nanorods were measured without further process after synthesis. Figure 3 shows Vis-IR absorption spectra of as-synthesized Au nanorods suspension with various amounts of 10 mM AgNO₃. In seed-mediated Au nanorods synthesis, the concentration of AgNO₃ solution determines the absorbance characteristics of Au nanorods resulting from their physical dimensions [20, 33]. There are two distinct peaks in the absorbance spectra. The peak near 507 nm is due to transverse resonance mode and the peak in NIR wavelength is longitudinal resonance mode. In this experiment, Au nanorods synthesized with 85 μ L 10 mM AgNO₃, which have longitudinal absorbance wavelength at around 815 nm, were used to match the wavelength of the NIR laser light source.

3.3 Photothermo response of bulk p-NIPAAm hydrogels with Au nanorod concentration

To study the Au nanorod concentration dependence of photothermal response of p-NIPAAm hydrogels, dome shape (volume: $\sim 0.5 \text{ cm}^3$) bulk p-NIPAAm hydrogels were prepared with various amount of Au nanorods, (a) pure p-NIPAAm hydrogel (b) p-NIPAAm hydrogel with Au nanorods from 4mL suspension (c) p-NIPAAm hydrogel with Au nanorods from 20 mL suspension and (d) p-NIPAAm hydrogel with Au nanorods from 24 mL suspension and shown in Fig. 4(a)–(d), respectively. Approximately 1 mg of Au nanorods is obtained from 10mL Au nanorod suspension by seed mediated Au nanorod synthesis procedure assuming 100% yield [33]. All bulk p-NIPAAm hydrogels show uniform dispersion of Au nanorods without aggregation. Fig. 4(e) shows temperature change as a function of illumination time on bulk p-NIPAAm hydrogels by illuminating 300mW 815 nm laser beam. The temperature at the spot of illumination was measured by the FLIR i7 compact infrared (IR) thermal imaging camera (FLIR system, USA). The pure p-NIPAAm hydrogel doesn't show any photothermal effect and the temperature stays constantly around 18 °C. For other bulk p-NIPAAm hydrogels containing Au nanorods, the temperature at the illumination spot increases gradually with illumination time and temperature increment stops at the maximum temperature after around 5 minutes of illumination for all three bulk hydrogels. The higher maximum temperature by photothermal effect was observed from the hydrogel, which contains the more amount of Au nanorods.

3.4 Photothermal response of p-NIPAAm hydrogel in a macroporous silicon membrane

Fig. 5(a) and (b) show the scanning electron microscope (SEM) images of completely opened 400 μ m thick microporous silicon membrane. Pores are periodically arranged with 12 μ m period and 64 μ m² pore opening.

To image the actuation of Au nanorods embedded hydrogel columns in macroporous silicon membrane by 815 nm NIR light, we built custom microscope setup as shown in Fig. 6. The setup can illuminate NIR light to the bottom of a sample, and capture optical images by inverted optical microscope. 400mW 815 nm NIR light was illuminated to the bottom of the silicon membrane filled with Au nanorods/p-NIPAAm hydrogel composite, and the real-time

image of transmitted light at the illuminating spot of 815nm NIR beam was captured. Fig. 7(a)–(d) show progressive image frames of a video captured with the illumination of NIR laser light (a) with 400 mW laser illumination, and turning off the laser power after (b) 0.1 sec., (c) 0.2 sec., and (d) 0.3 sec. The green-circled area in Fig. 7(a)–(d) represents NIR illuminated area. When the NIR light is illuminated to the macroporous silicon membrane filled with Au nanorods/p-NIPAAm hydrogel composite, Au nanorods embedded in p-NIPAAm hydrogel absorb light energy and convert to heat by SPR effect, and raise the temperature of p-NIPAAm hydrogel above the LCST ($\sim 34^{\circ}\text{C}$). Consequently, the transparency of p-NIPAAm hydrogel columns changes to opaque, and the transmission of broadband light is blocked appeared as dark spots over the NIR illuminated area shown in Fig. 7(a). Once the NIR light is switched off, the temperature of the p-NIPAAm hydrogel is lowered below the LCST, and the transparency of p-NIPAAm hydrogel columns is reverted to transparent allowing transmission of broadband light shown as bright spots in Fig. 7(b)–(d).

We also investigated photothermal transient behavior of p-NIPAAm hydrogel columns in the macroporous silicon membrane. Fig. 8 shows transmitted light intensity change as a function of time through macroporous silicon membrane while switching the laser power (Supplementary material, Video 1). The intensity of transmitted light was calculated by summing up the brightness values of pixels in the green circle from captured video with time interval of 0.1 second. The optical transition behavior by reversible optical transition of p-NIPAAm hydrogel columns actuated by NIR light shows very fast response in both heating phase (the transition from transparent state to opaque state) and cooling phase (the transition from opaque state to transparent state) in less than 300 msec, unlike bulk Au nanorods embedded p-NIPAAm hydrogel, which requires more than 2 minutes to undergo phase transition by NIR illumination. In addition, the repeated switching behaviors of heating and cooling cycles are almost identical over the multiple switching cycles, which implies robust and repeatable switching mechanism of p-NIPAAm hydrogel columns by the photothermal effect.

4. Conclusion

We have demonstrated rapid photothermal response of Au nanorod embedded hydrogel columns confined in a macroporous silicon membrane. Surface plasmon-induced thermal heating of Au nanorods using NIR light was incorporated in temperature-sensitive p-NIPAAm hydrogel. Optical transmission through the membrane was utilized to monitor the hydrogel photothermal actuation. The measured optical transmission through the fabricated structure demonstrates a potential application of highly localized, photothermal actuation of the implemented hydrogel columns with sub-second response time. Considering that the strong optical absorption of Au nanorods depends on their physical dimension, a wide range of light sources can be used to independently actuate p-NIPAAm hydrogel implemented in our structure. Furthermore, based on the optical control approach, individual pores or a group of pores can be individually or locally actuated without any physical connections. Through the unique volume change of p-NIPAAm by temperature stimulation, the presented structure has a potential for novel drug release systems that require a rapid response with remote optical control.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Biography

Youngsik Song received the B.E degree in electronics engineering from Dankook University, Korea, M.S. degree in electrical engineering from Louisiana State University, and Ph.D. degree in electrical engineering from Wayne State University. He was post doctoral scholar at the University of Kentucky, Lexington, KY and research scientist at the University of Arizona, Tucson, AZ. His research interests are in the area of nanomaterials and their applications in electronics and photonics.

Hojjat Rostami Azmand received the B.S. and M.S degree in electrical engineering from University of Tabriz in 2011 and 2013 respectively. He started his PhD at the City College of New York in 2015. His research interest is to develop compact optical sensors, fabrication of polymer based photonic devices, semiconductor processing, and optical resonators.

Sang-Woo Seo received B.S. degree in electrical engineering from Ajou University, M.S. degree from the Kwangju Institute of Science and Technology, South Korea, and Ph.D. degree in electrical engineering from the Georgia Institute of Technology, USA, in 1997, 1999, and 2003, respectively. In 2007, he joined the Department of Electrical Engineering, City College, New York, NY, USA, where is currently an Associate Professor. His current research interests include heterogeneous optoelectronic device integration, integrated microfluidic/photonic sensors, integrated THz systems, bioMEMs, and optical micromechanical systems.

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Highlights

- Temperature responsive p-NIPAAm hydrogel incorporated with gold nanorods forms micro-sized arrayed columns in a macroporous silicon membrane.
- Near infrared light as stimulus is used to generate local heating by surface plasmon resonance of Au nanorods embedded in p-NIPAAm hydrogel columns.
- Very fast photothermal response time less than 300 msec. and repeatable actuation of thermos-responsive hydrogel columns on highly localized illuminated area were achieved.

Figure 1. Schematic diagrams of (a) Au nanorods/p-NIPAAm hydrogel composite in a macroporous silicon membrane below lower critical solution temperature (LCST), (Au nanorod/hydrogel composite: pink, silicon membrane: gray, silicon dioxide: yellow) (b) Operation of NIR light actuated macroporous silicon membrane filled with Au nanorods/p-NIPAAm hydrogel composite (white: deswelled opaque p-NIPAAm hydrogel by photothermal actuation by NIR light illumination)

Figure 2.

(a) Pure p-NIPAAm hydrogel in a glass capillary tube at 19 °C, (b) Pure p-NIPAAm hydrogel in a glass capillary tube at 40 °C, (c) Schematic diagram of custom built Thermo-optical transmission measurement setup for p-NIPAAm hydrogel. (d) Thermo-optical transmission characteristic of p-NIPAAm hydrogel in a glass capillary tube, showing LCST at about 34 °C, (heating cycle: red, cooling cycle: blue)

Figure 3. Transmission spectra of Au nanorods synthesized with various amount of 10 mM AgNO₃ solution. By controlling the amount of AgNO₃ during Au nanorod synthesis, the longitudinal SPR band can be adjusted.

(e)

Figure 4.

Images of bulk p-NIPAAm hydrogel. (a) Pure hydrogel, and hydrogels containing various amount of Au nanorods from (b) 2 mL suspension (c) 20 mL suspension (d) 24 mL suspension. (e) Photothermo response behavior of bulk p-NIPAAm hydrogels with different Au nanorod concentrations.

(a)

(b)

Figure 5. Scanning Electron Microscopy images of a macroporous silicon membrane, (a) Top view, and (b) Cross-section view

Figure 6.
Schematic diagram of the custom built actuation - measurement setup for observing optical transmission actuated by NIR light

Figure 7.

Progressive image frames of the macroporous silicon membrane (green circle area represents NIR laser illumination area) (a) Blocked transmitted light as dark spots with 400mW NIR laser illumination (above the LCST of p-NIPAAm hydrogel columns), (b) Transmitted light 0.1 seconds after turning off the 400mW NIR laser power, (c) Transmitted light 0.2 seconds after turning off the 400mW NIR laser power, and (d) Transmitted light 0.3 seconds after turning on the 400mW NIR laser power

Figure 8.
Transmitted light intensity as a function of time by repeated NIR laser power switching shows fast on-off transition and reliable response over multiple switching cycles