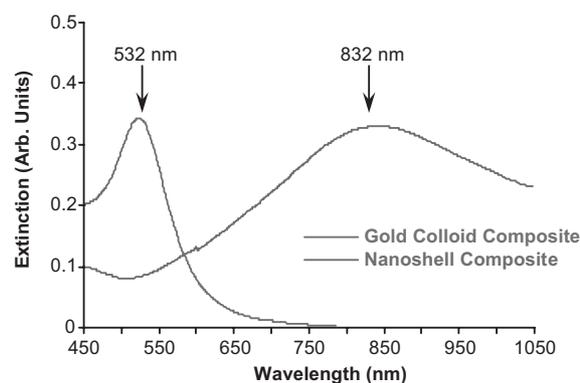# Independent Optical Control of Microfluidic Valves Formed from Optomechanically Responsive Nanocomposite Hydrogels**

By *Scott R. Sershen, Glennys A. Mensing, Marie Ng, Naomi J. Halas, David J. Beebe,* and *Jennifer L. West**

The ability to actively manipulate fluid-flow patterns through microfluidic devices is important to many current applications and vital to the development of more complex systems in the future. A typical actively controlled valve developed to date consists of a flexible diaphragm coupled to an electromagnetic, electrostatic, or thermopneumatic actuator.[1] Design of an air-driven membrane valve has also been reported.[2] Despite this progress, there remains a significant need for materials that allow easy and controlled manipulation of valves and actuators in microfabricated devices, and ideally, independent control over multiple components within a single device.

Recently, pH-responsive hydrogel materials have been used as valves in microfluidics devices.[3,4] This has allowed control of flow based on local environmental conditions (e.g., pH), which is attractive for some applications due to the simplicity of the system design. This work demonstrated the feasibility of forming hydrogel valves in microfluidic devices via photopolymerization and of utilizing hydrogels that undergo shape changes in response to stimuli as controllable valves or actuators. However, using pH as a control mechanism limits the number of components that can be independently controlled and requires that all components of the system be compatible with the requisite changes in pH. Many microfluidics applications will not be compatible with a wide range of pH conditions. Furthermore, for some applications it would be advantageous to have independent external control of valve operation, which would be difficult to achieve with pH-responsive materials. In the current system, dramatic changes in material size and shape can instead be induced by exposure to specific wavelengths of light. The use of light as a stimulus is particularly attractive as it is easily directed to specific locations within a channel network, possibly allowing further control.

To accomplish this, we have developed materials that undergo pronounced and reversible changes in shape and size in response to different wavelengths of light. These materials are composites of a thermally responsive polymer (poly[*N*-isopropylacrylamide-*co*-acrylamide] with a 95:5 comonomer ratio) and particles that have distinct and strong optical-absorption profiles (gold colloids and nanoshells). The gold colloid was formed using the method of Duff et al.,[5] while gold nanoshells with a 110 nm diameter silica core and 10 nm thick gold shell were synthesized as described by Oldenburg et al.[6] The absorption spectra of these two nanomaterials are shown in Figure 1. The composites were formed by mixing the nanoparticles with the monomer solution, thus entrapping the particles within the hydrogel matrix after polymerization. These nanocomposite materials respond to different wavelengths of

Figure 1. Extinction spectra for the gold colloid and gold nanoshells used to form nanocomposite hydrogels. These metal nanoparticles were chosen to match the output of the two lasers used for optical control of the microfluidics valves, one at 532 nm and one at 832 nm.

light (Fig. 2); in this example, one nanocomposite material collapses in response to green light (gold-colloid nanocomposite hydrogel) while the other collapses in response to near-IR light (gold-nanoshell nanocomposite hydrogel). It should be noted that while the response time of these macroscale hydrogels is slow, the response time is diffusion limited and thus scales with size so that the microscale valve materials respond much more quickly. This ability to create differentially controllable materials can allow one to have a series of valves or actuators, for instance in a microfluidics chamber or other type of microfabricated device, which could be activated by changing the wavelength of light used to illuminate the device. Differential control could be achieved either by using multiple materials sensitive to different wavelengths, by using one material with light directed to specific areas of the chip, or a combination of these approaches.

We have demonstrated independent control of two valves at a junction within a microfluidic device. Nanocomposite-hydrogel valves were formed by photopolymerizing the monomer mixture, with the inclusion of the appropriate nanoparticles, within a microfluidic device at a T-junction using a

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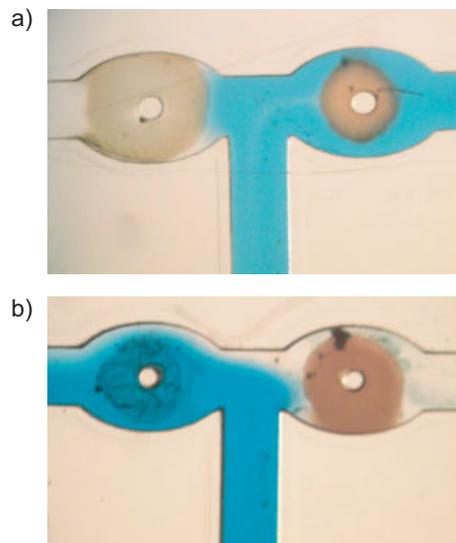Houston, TX 77251 (USA)
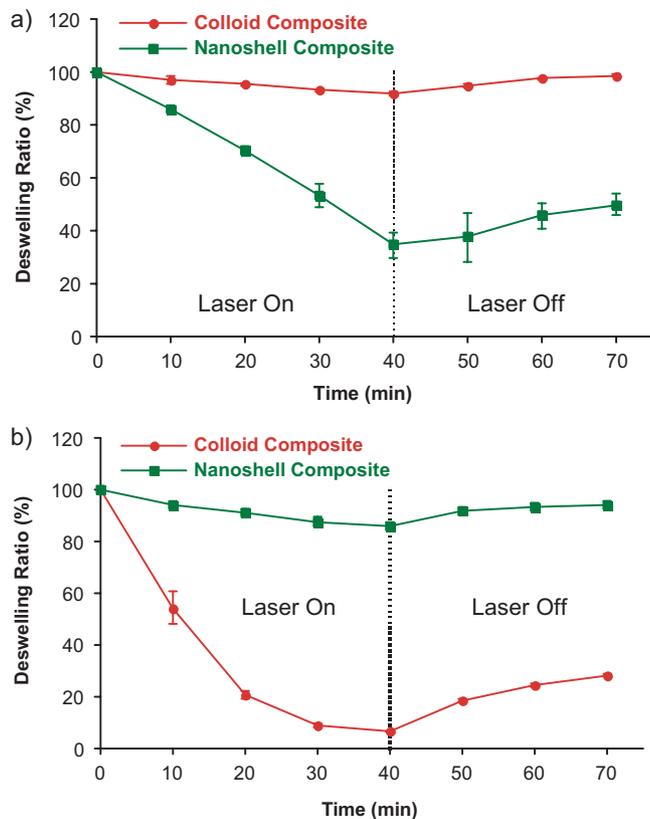
Figure 2. The collapse and reswelling of the gold-colloid composite hydrogels (red circles) and gold-nanoshell composite hydrogels (green squares) during and after 40 min of irradiation at a) 832 nm (2.7 W cm²) or b) 532 nm (1.6 W cm²). Data are the mean deswelling ratios and the error bars are standard errors of the mean.

Figure 3. Two valves formed at a T-junction in a microfluidics device, one made of a gold-colloid nanocomposite hydrogel and the other a gold-nanoshell nanocomposite hydrogel. The channels are 100 μm wide. a) When the entire device was illuminated with green light (532 nm, 1.6 W cm⁻²), the gold colloid valve opened while the nanoshell valve remained closed. b) However, when the device was illuminated with near infrared light (832 nm, 2.7 W cm⁻²), the opposite response was observed. In both cases, the valves opened within 5 s.

photomask to limit conversion of monomer to polymer at the desired valve location. After forming one valve at the junction, the system was rinsed, filled with monomer with the second nanomaterial, and the photopolymerization process was repeated over a post at the other side of the junction. After thoroughly rinsing the device, a solution of blue dextran was introduced to allow visualization of the flow patterns obtained under different conditions. The entire device was illuminated with either green light (532 nm, 1.6 W cm⁻², Coherent) or near-IR light (832 nm, 2.7 W cm⁻², Coherent). The valve diameters were monitored during illumination, as was the fluid-flow pattern. Only the gold-colloid nanocomposite hydrogel valve opened during illumination with green light, while only the gold nanoshell-containing valve responded to near-IR light (Fig. 3). In both cases, the valves opened completely in less than five seconds. If required, even faster responses could be obtained with higher light intensities. Additionally, phase changes in these thermally responsive hydrogel materials are completely reversible,[7] allowing repetitive cycling of a valve.

In this initial study, we have demonstrated independent control of two valves. However, it is theoretically possible to independently control a large number of components simply by choosing nanoparticles with appropriate absorption spectra

or by utilizing directed light (e.g. micromirror arrays), or both. Additionally, the lower critical solution temperature (LCST) of the temperature-responsive material could be tailored by altering the copolymer composition. By raising the LCST, one could also use absorbing materials with slightly overlapping absorption curves, since slight heating in non-targeted valve materials would not result in a phase change, allowing the valve to remain closed. Nanoshells are particularly attractive for such a system since their optical absorption can be tuned across the visible, near-, and mid-IR regions of the electromagnetic spectrum,[6,8] allowing generation of a broad range of nanomaterials with separated absorption spectra. This may allow one to incorporate many independently controlled components within a single device.

Experimental

Nanoparticle Synthesis: Citrate gold colloid was formed using the method of Duff et al. [5]. 469 mg of sodium citrate was brought to a boil in 742 mL deionized (DI) water. 7 mL of 27 mM HAuCl₄ was added, and the solution was boiled for an additional 15 min. Gold colloid was concentrated by centrifugation. Gold nanoshells were formed using the methods of Oldenburg et al. [6]. Silica cores with a mean diameter of 110 nm were formed using the Stober process. The surfaces of the silica particles were terminated with amine groups via reaction with aminopropyl triethoxysilane. The gold colloid (1–2 nm in diameter) was allowed to adsorb to the amine groups on the silica particles.

These were then used as nucleation sites for formaldehyde-initiated reduction of gold from $HAuCl_4$ to form a complete shell. Nanoparticles were characterized via transmission electron microscopy and UV-vis spectroscopy.

To stabilize the nanoparticles before inclusion in hydrogels, their surfaces were modified with PEG-thiol. $PEG-NH_2$ (molecular weight 5000 g mol^{-1}) was reacted with a tenfold excess of Traut's reagent for 1 h at room temperature to form PEG-thiol. The product was dialyzed against DI water to remove excess Traut's reagent.

Formation of Nanocomposite Hydrogels: A 1.75 M monomer solution containing *N*-isopropylacrylamide and acrylamide in a 95:5 molar ratio was prepared, and the crosslinker *N,N′*-methylenebisacrylamide was added at a 1:750 molar ratio. The appropriate nanoparticle suspension (gold colloid or gold nanoshells, both PEGylated) was added and mixed well with the monomer solution. 1500 ppm 2,2-dimethoxy-2-phenylacetophenone was added as the photoinitiator. Long-wavelength UV light was then used to form hydrogels. For studies with microfluidics devices [3], the devices were filled with the gold-colloid-containing monomer solution, and a photomask was used to limit photopolymerization to the desired location. Photomasks were prepared by printing patterns on transparency films using a high-resolution printer (Linotype Herkules Imagesetter, 5080 dpi). Under a microscope, the mask was placed at the T-junction over a post designed to hold the resultant hydrogel valve in place upon collapse of the material, and the system was exposed to UV light to polymerize the hydrogel valve. The system was then rinsed thoroughly with DI water, and the process repeated with gold-nanoshell-containing monomer to form a valve at the other side of the T-junction.

Evaluation of Light-Induced Phase Changes: Hydrogel disks containing either gold colloid or gold nanoshells were incubated in *N*-(2-hydroxyethyl)piperazine-*N′*-(2-ethanesulfonic acid) (HEPES) buffered saline and exposed to green light (532 nm, 1.6 W cm^{-2}, Coherent, matching the absorbance of gold colloid) or near-IR light (832 nm, 2.7 W cm^{-2}, Coherent, matching the absorbance of gold nanoshells). At predetermined time points, the disks were removed and weighed to determine the degree of deswelling.

Optically Controlled Valves: To evaluate the controlled manipulation of nanocomposite hydrogel valves with light, the entire microfluidic chip was exposed to either green light (532 nm, 1.6 W cm^{-2}, Coherent) or near-IR light (832 nm, 2.7 W cm^{-2}, Coherent) while visualizing the T-junction using an Axiovert 135 microscope (Zeiss). Blue dextran was infused to allow visualization of the flow pattern. The valve diameter was monitored during illumination.

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A Full-Color Electroluminescent Device and Patterned Photoalignment Using Light-Emitting Liquid Crystals**

By *Matthew P. Aldred*, *Adam E. A. Contoret*, *Simon R. Farrar*, *Stephen M. Kelly*,* *Dean Mathieson*, *Mary O'Neill*,* *Wing C. Tsoi*, and *Panos Vlachos*

The invention of the first stable, room-temperature, nematic liquid crystal at Hull in the early 1970s led to the widespread use of liquid-crystal displays (LCDs),[1] which achieve full color by transmission of white light through pixels of color filters and polarizers. As little as 1 % of the light generated was transmitted. Organic light-emitting diodes (OLEDs), which emit colored light by electroluminescence (EL), have entered the flat-panel display marketplace as they are intrinsically brighter, faster, and more legible over wider viewing angles than LCDs.[2,3] A variety of methods has been used to obtain high-resolution full-color OLEDs, which require regular arrays of separate red, green, and blue pixels: thermal evaporation of small molecules through shadow masks,[4] high-resolution inkjet printing of light-emitting polymers (LEPs),[5,6] screen printing,[7] and color conversion of white light through glass filters.[8] Photochemical crosslinking of LEPs is an attractive alternative approach to creating insoluble polymer network films[9–11] and a multicolor polymer OLED has recently been demonstrated using photolithography.[12] Polymerization of light-emitting liquid-crystalline monomers, so-called reactive mesogens (RMs),[13–18] may be an even more promising route to full-color displays, as the self-assembling nature of liquid crystals gives improved carrier mobility[19,20] and polarized emission when uniformly aligned.[15,21,22] The latter property can provide improved viewing in bright-light conditions. RMs have added advantages over non-polymerizable LCs, in that the solution processing of multilayer devices is possible by photopolymerization of the underlying layers. We found that optimal UV exposure, without a photoinitiator, of a light-emitting, nematic RM with non-conjugated diene end groups gives insoluble and non-meltable polymer networks with minimal photodegradation of the chromophore, and no observable cracking of the polymer layers.[15,23] The photoluminescence quantum

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