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COMMUNICATION

Polymer Brush-Based Optical Device with Multiple Responsivities

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Poly N-isopropylacrylamide-co-acrylic acid (pNIPAm-co-AAc) polymer brushes were grown from Au-coated glass substrates via surface initiated atom transfer radical polymerization (SI-ATRP). Subsequently, another thin Au layer was deposited on top of the brush to yield a sandwich structure, with the brush confined between the two Au layers. This structure was shown to exhibit excellent optical properties and shows a response to multiple external stimuli, such as pH, temperature and humidity. This novel device could be used for sensing, biosensing, drug delivery, or for other applications that require light manipulation and wavelength filtration.

Since the pioneering work of Yablonovitch¹ and John² in 1987, photonic materials have attracted significant attention. These materials possess periodic refractive index variability and can be classified as one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D), depending on if their periodicity is in 1, 2, or 3 dimensions, respectively. Photonic materials have found many uses and applications, e.g., optical fibers,³ photovoltaic devices,⁴ displays,⁵ and sensors.⁶ While photonic materials in general are of great interest, structures that change their optical properties in response to stimuli only increase their utility. Previously, a number of materials have been used to fabricate these devices. Among them, responsive polymer-based photonic structures⁷ have emerged as some of the most useful.⁸ Structures have been made that respond to stimuli such as pH,⁹

ionic strength,^{6a} solvent,¹⁰ and electric¹¹ and magnetic fields.¹² In our previous studies, we demonstrated that poly (N-isopropylacrylamide) (pNIPAm)-based hydrogel particles (microgels) could be used to fabricate tunable photonic materials.¹³

PNIPAm has received significant attention over the years due to its thermally switchable solubility and conformation in water.¹⁴ Specifically, in water of a temperature lower than pNIPAm's lower critical solution temperature (LCST) of 32 °C, it is fully soluble and exists as a random coil, while pNIPAm collapses and becomes insoluble when the temperature >32 °C. PNIPAm has been used for a variety of applications including: separations,¹⁵ biotechnology,¹⁶ actuation¹⁷ and tissue engineering.¹⁸ As mentioned above, pNIPAm can exist as a random coil in solution, while it can also be crosslinked into network structures to make hydrogels and hydrogel particles (microgels).¹⁹

In this submission, we synthesize pNIPAm-based brushes on surfaces. Polymer brushes are polymer chains tethered to a surface or interface via physisorption²⁰ or covalent attachment.²¹ Physisorption involves the adsorption of polymer chains on a surface or interface, although the polymer attachment can be weakened at high temperature and upon solvent replacement.^{20, 22} To yield a more robust film, covalent attachment can be used. This can be achieved via "grafting to" or "grafting from" techniques.²³ The "grafting to" method involves polymers diffusing to the substrate surface, and reacting with a surface functional group. The "grafting from" approach uses a surface that has a reactive group, e.g., initiator or monomer, covalently attached to a surface, which can be

polymerized. In this case the thickness of the polymer film can be controlled by varying the polymerization time. One of the most common polymerization methods used for "grafting from" is atom transfer radical polymerization (ATRP).²⁴ Compared to traditional radical polymerizations, it provides control of polymer chain elongation, which gives narrow polydispersity index (PDI) and controlled molecular weight. In this way, the thickness of polymer brushes can be controlled.²⁵

In this communication we used a "grafting from" approach to generate a pNIPAm brush layer on a Au-coated glass substrate, then deposited another thin Au layer on top of the resultant brush to make a "sandwich" structure. The Au layers were deposited via thermal evaporation, while the rest of the device construction details are given in the electronic supporting information (ESI). This device yields bright visual color, which could be tuned by adjusting the thickness of polymer brush. Furthermore, the devices could change their color dynamically by temperature changes, i.e., tuning the pNIPAm solvation state allowed the brush thickness to be dynamically tuned, therefore changing the visual color. Additionally, we made the pNIPAm layer pH responsive by copolymerization of acrylic acid (AAc) into the pNIPAm layer, and its pH response was characterized. Finally, we investigated the device's response to humidity.

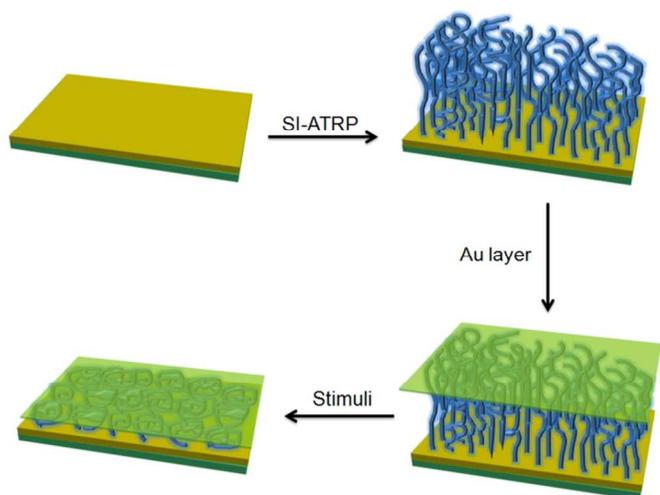


Fig. 1 Illustration of the device fabrication process and its response to a stimulus.

Initially, pNIPAm-based brushes were grown onto Au-coated glass substrates, as shown in Fig. 1. First, an ATRP initiator was attached to the Au surface by a self-assembly process in anhydrous ethanol. Following this step, surface-initiated atom transfer radical polymerization (SI-ATRP)^{21a, 24b} was conducted to produce the desired brush. The resultant brush was characterized by ellipsometry and atomic force microscopy (AFM). Ellipsometry revealed that the thickness could be tuned over 300 nm, while AFM shows that the RMS roughness is ~ 3 nm. The images can be seen in ESI. Finally, another 15 nm Au layer was thermally evaporated onto the resultant polymer brush. This yields a layered structure, which is capable of interacting with light to produce color. Specifically, light

is capable of entering the brush-based cavity and undergoes multiple reflections, yielding constructive and destructive interference. This interference allows specific wavelengths of light to be reflected/transmitted, yielding color. The specific wavelengths that are reflected can be predicted from equation 1:

$$m\lambda = 2nd \cos \theta \quad (1)$$

where λ is the wavelength maximum of the reflected peak/peaks, m is the peak order, n is the refractive index of the dielectric medium, d is the distance between the two layers of Au, θ is the incident angle. From the equation, we see that wavelength is directly proportional to the distance between these two layers of Au. Since the distance can be tuned by the pNIPAm brush responsivity, the position of the device's reflectance peaks and its color can be dynamically tuned.

Etalons composed of a variety of brush thicknesses were fabricated, and the optical properties investigated. As shown in Fig. 2, when white light is exposed to the devices, specific wavelengths of light are reflected dictated by the brush thickness. The device is also visually colored, as can be seen in ESI. As can be seen, as the brush thickness of the brush is increased, the number of peaks in the reflectance spectrum increases. This is a direct result of more orders of reflection being possible when the etalons dielectric thickness increases, as can be predicted from equation 1.

To investigate the ability of these devices to respond to multiple stimuli, we prepared pNIPAm-based brushes with and without acrylic acid (AAc). The various responsivities are shown in Fig. 3. First, a pNIPAm brush-based device was generated, and its response to temperature investigated. In this case, the device was investigated using reflectance spectroscopy (as in Fig. 2), and the position of a single wavelength monitored as an indicator of its response. As can be seen in Fig. 3a, the device's reflectance peak shifted an impressive ~ 500 nm when the water temperature was changed from 24 to 40 °C. Additionally, the visible color of the device changed dramatically, see ESI. The response is a direct result of the pNIPAm brush layer collapsing at $T > LCST$, bringing the device's Au layers close to one another. The response was shown to be reversible over many cycles, see ESI.

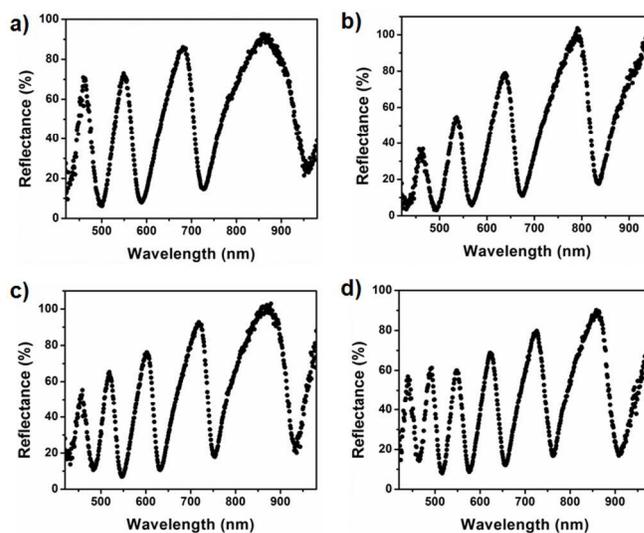


Fig. 2 Reflectance spectra for pNIPAm polymer brush-based devices with brush thicknesses of: a) 237 ± 9 nm, b) 289 ± 9 nm, c) 380 ± 10 nm, and d) 441 ± 6 nm. The thicknesses were measured using AFM (see ESI).

In addition to the temperature response, we investigated the pH response for the AAc-modified brushes. As AAc exhibits a pK_a value of ~ 4.25 , it is deprotonated, and negatively charged at $pH > 4.25$, while it is neutral at $pH < 4.25$. Coulombic repulsion of negative charges at $pH > 4.25$ causes the polymer brush to expand, which increases the distance between these two layers of Au. This response is expected to yield a red shift of the reflectance peaks. While protonation of the AAc groups should cause the polymer to contract, and yield a blue shift in the reflectance spectrum peaks. As can be seen in Fig. 3b, the reflectance peaks red shift from 440 nm to 570 nm as the pH is raised above AAc's pK_a , and goes back to the original position once the pH is returned to < 4.25 . The pH response is also reproducible over many cycles (see ESI). We also investigated the temperature response at both high and low pH. At $pH 2.44$, the wavelength shifted from 800 nm to 600 nm as temperature was increased from 22 to 34 °C. As can be seen, the transition temperature for these devices is lower than the devices without AAc as a result of the increased hydrophilicity of the brush due to the AAc groups. At $pH 6.50$ (above AAc pK_a), the wavelength shifts from 600 nm to 500 nm when temperature is increased from 24 to 40 °C. The minimal temperature responsivity is a result of the negative charges in the brush preventing the collapse at high temperature.

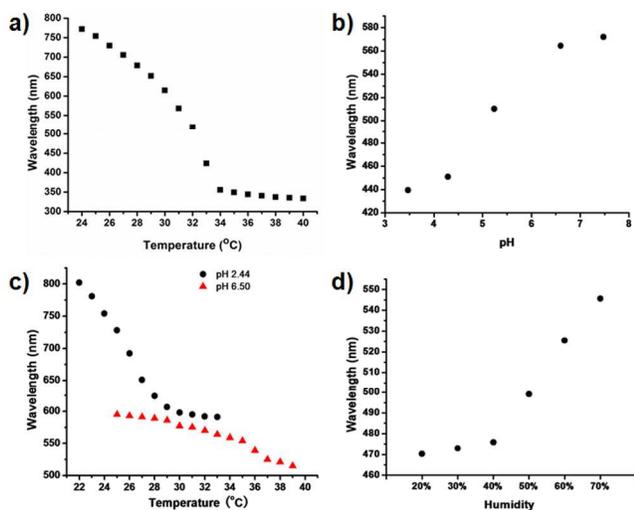


Fig. 3 Stimuli responsive properties of polymer brush-based devices. a) Temperature responsivity of pNIPAm brush-based device; b) pH responsivity of pNIPAm-co-AAc brush-based device; c) Temperature responsivity of pNIPAm-co-AAc brush based device at the indicated solution pH; d) Humidity responsivity of pNIPAm-co-AAc brush based device.

Finally, we demonstrated that the pNIPAm-co-AAc brush-based devices exhibit optical responses to atmospheric humidity changes. As shown in Fig. 3d, the wavelength shifts from 470 nm to 550 nm as the relative humidity increases. As can be seen, the device

is extremely sensitive to humidity once the humidity reaches 40 %. We hypothesize that the red shift is observed due to the polymer chains hydrating at high humidity, while they dehydrate (and collapse) at low humidity. This is a result of the hygroscopic properties of the pNIPAm-based brush.

In conclusion, we constructed a stimuli-responsive optical device that changes its optical properties in response to multiple environmental stimuli, including temperature, pH and humidity. The device's responsivity is a direct result of the pNIPAm-based layer changing conformation when exposed to these stimuli, which directly changes the distance between the device's Au layers. The device is easily prepared using standard ATRP polymerization, and is extremely versatile regarding the functionality that can be added to the brush layer. For example, by reacting the resultant AAc groups with other functional molecules, the brush can exhibit responses to other stimuli and can be used for sensing or drug delivery applications.

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Notes and references

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Poly (*N*-Isopropylacrylamide) brush-based optical materials were fabricated, and the tunability of their optical properties characterized

