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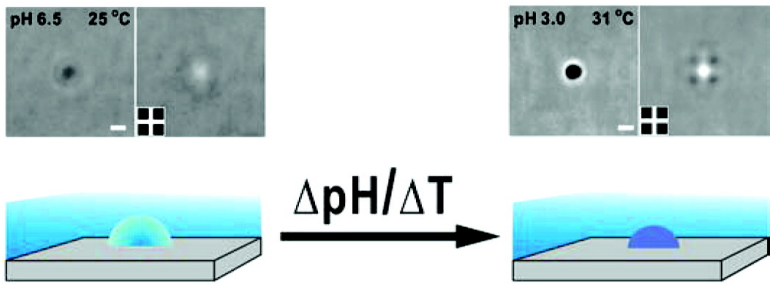

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Hydrogel Microparticles as Dynamically Tunable Microlenses

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Microlens array technology has gained in interest over the past decade for applications in optical imaging systems,[1,2] optical communications,[3] and photolithography.[4,5] Fabrication of microlens elements has previously been achieved via photolithography,[6] photodecomposition,[7] photothermal patterning,[8] and particle self-assembly/melting.[9] While the above technologies have been successful in achieving functional micro-optics, the particular issue of creating a dynamically tunable microlens via application of an external stimulus remains a challenge. Realization of dynamically tunable microlens elements would increase the potential for microlens arrays in foveated vision, chemical sensing, and beam steering.

Poly(*N*-isopropylacrylamide) hydrogels are materials that can respond to external stimuli such as temperature, pH, ionic strength, electric field,[10,11] and antibody−antigen interactions[12] by swelling/shrinking transitions. It has been shown by our group[13,14] and others[15,16] that stimuli-responsive particles composed of this material and copolymers thereof can be easily synthesized. The fact that these materials are stimuli responsive makes them excellent candidates for use in dynamically tunable microlens structures. Microlens arrays can be fabricated by assembling poly(*N*-isopropylacrylamide-*co*-acrylic acid) (pNIPAm-AAc) microgels onto a 3-aminopropyltrimethoxysilane (APTMS)-functionalized glass substrate through an electrostatic self-assembly method.[17] An example of an ordered microlens array is shown in Figure 1. Plano-convex lens formation is due to deformation of the microgels in an anisotropic fashion during substrate attachment due to the mechanical softness of microgels. Here, we demonstrate that such microlens arrays are able to project images in aqueous environments and are dynamically tunable. Note that the analysis of single-lens elements is presented and that full arrays behave similarly (see Supporting Information).

For this investigation, ~2-μm diameter pNIPAm-AAc microgels were synthesized as described previously.[13,14,18] These microgels were used to fabricate microlenses by adding a drop of an aqueous 10% (v/v) microgel solution at pH 6.5 to an APTMS-functionalized glass substrate. At this pH, the microgels are anionic, allowing for good adhesion to the cationic substrate. The substrate was allowed to dry for 24 h at room temperature followed by immersion in deionized water for 2 h. The substrate was then rinsed with deionized water to leave behind only the microgels strongly attached to the substrate by electrostatic interaction. Dynamic tunability of the microlenses in response to pH was illustrated by introducing different pH solutions into the void space in a microlens/silicone gasket/coverslip sandwich assembly (Scheme 1) using syringes inserted through the wall of the gasket. To perform optical measurements, an Olympus IX-70 inverted optical microscope was used in the arrangement shown in Scheme 1, as described previously.[17] The microscope was equipped with a microscope objective heater and a Peltier-based temperature stage.

Figure 2 shows the focal length tunability of a single microlens in response to pH at 25 °C. The differential interference contrast

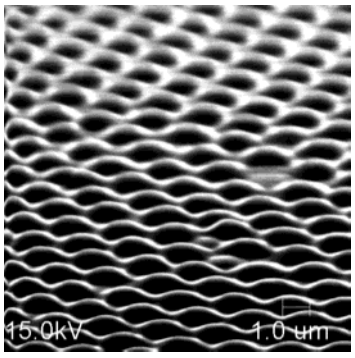


Figure 1. SEM image of a microlens array imaged at a grazing angle with respect to the substrate. The microgels have formed an ordered array of plano-convex shapes.

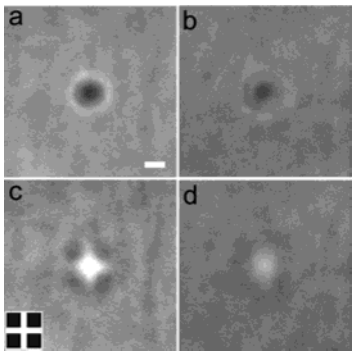
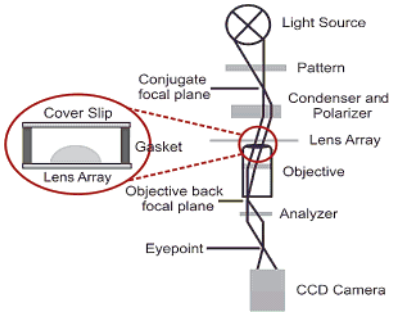


Figure 2. DIC microscopy images of a substrate-bound microgel at pH 3.0 (a) and 6.5 (b) at 25 °C. Panels (c) and (d) show the projection of the cross-like pattern (inset) through the microgel at the respective pH values. The scale bar is 1 μm.

Scheme 1. Microscopy Setup Used for Aqueous Imaging Experiments[a]



[a] The lenses at the image plane move the objective back focal plane to the eyepoint thus, bringing the pattern near the source into focus.

(DIC) images in panels (a) and (b) show that the substrate-bound microgel is compact at pH 3.0 and swollen at pH 6.5, respectively. This behavior is due to the AAc groups within the microgel network becoming negatively charged ($pK_a \approx 4.25$) at pH 6.5, which in turn causes gel swelling due to Coulombic repulsion and osmotic

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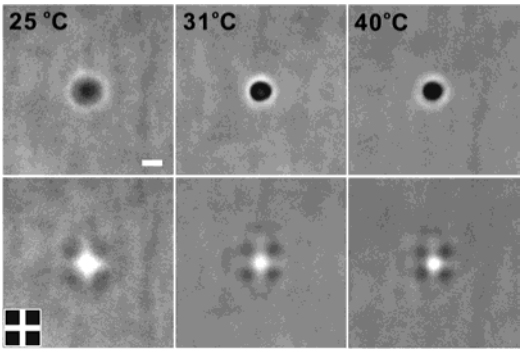

Figure 3. (Top) DIC microscopy of a substrate bound microgel in pH 3.0 solution versus temperature. (Bottom) Projection of the cross-like pattern (inset) through the same microgel. The scale bar is 1 μm.

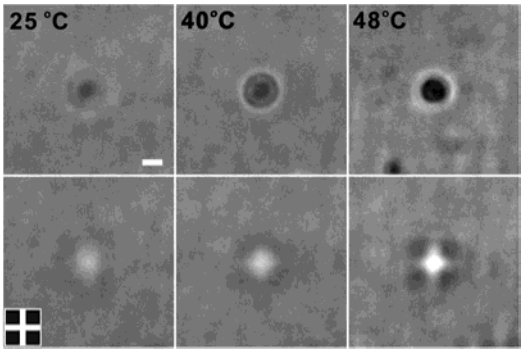

Figure 4. (Top) DIC microscopy of a substrate-bound microgel in pH 6.5 solution versus temperature. (Bottom) Projection of a cross-like pattern (inset) through the same microgel. The scale bar is 1 μm.

effects.[15,16] Since the diameter and, presumably, the curvature of the substrate-bound microgels are tunable in response to pH, the lens power should be similarly tunable. This lens power tunability is illustrated in Figure 2(panels c,d) at pH 3.0 and 6.5, respectively. Panel (c) shows that the microgel at pH 3.0 brings into focus a cross-like pattern placed conjugate to the objective back focal plane,[17] while panel (d) shows that the same microgel at pH 6.5 is not able to focus the cross-like pattern at the same focal point. This focal length tunability can be understood by considering the microgels to be more optically dense at pH 3.0 than at pH 6.5. Taking into account the fact that focal lengths are dependent upon the ratio of the refractive index (RI) between the lens material and the surrounding medium, where a higher RI difference gives a lens with a shorter focal length (higher lensing power), it is clear why the cross-like pattern is visible through the microlens at pH 3.0 and is not focused at pH 6.5. Estimates as to the microgel dimension and refractive index changes that lead to these effects are presented in Supporting Information.

Since pNIPAm-AAc microgels are thermoresponsive at pH 3.0 but significantly less so at pH 6.5, the microlenses should display a pH-dependent thermal tunability. Figures 3 and 4 show the responsivity of the substrate-bound microgels and their resulting lensing ability as a function of temperature at pH 3.0 and 6.5, respectively. The DIC microscopy images in Figure 3(top) show that the microgels respond to increases in temperature by decreasing in size. This shrinking results in an increase in RI contrast with respect to water, which should result in an improved microlens structure. Figure 3(bottom), illustrates that this is the case. As the temperature is increased from 25 to 40 °C, the microlens focuses the cross-like pattern with higher fidelity. It is also interesting to note that the hydrogel undergoes a sharp transition at ∼31 °C,[13,14,19] which is the same point at which the microlens drastically changes its lensing ability. Figure 4(top) shows the DIC images of the substrate-bound microgel at pH 6.5 as a function of temperature. In contrast to the behavior at pH 3.0, the higher pH results in a microgel that is not responsive to heating over the same temperature range. It is not until 48 °C that the microgel undergoes a transition, which is consistent with previous studies of gel swelling.[13] As expected, the lensing ability, which is shown in Figure 4(bottom), is unaffected until the transition temperature of 48 °C, at which point the optical properties drastically change.

In conclusion, optical microscopy has been employed to show that substrate-supported, stimuli-responsive pNIPAm-AAc microgels form dynamically tunable microlenses. The lenses are produced via aqueous-phase polymerization, and the arrays are fabricated without photolithographic or micromolding processes. These characteristics make this system attractive for rapid construction of lens arrays with wet chemical methods. Furthermore, these structures are tunable as a function of temperature and pH, where the water content of the microgel has a profound effect on lensing ability due to changes in refractive index contrast with the medium. Given the intrinsically fast (sub-millisecond) shrinking rates of microgels, the ultimate tuning rates of such arrays could be similarly rapid. Together, this represents the first demonstration of dynamically tunable microlenses that are truly scalable to high-density array formats.

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Supporting Information Available: Expanded versions of Figures 3 and 4, images of particle arrays, and the Experimental Section. This material is available free of charge via the Internet at http://pubs.acs.org.

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