

Experimental

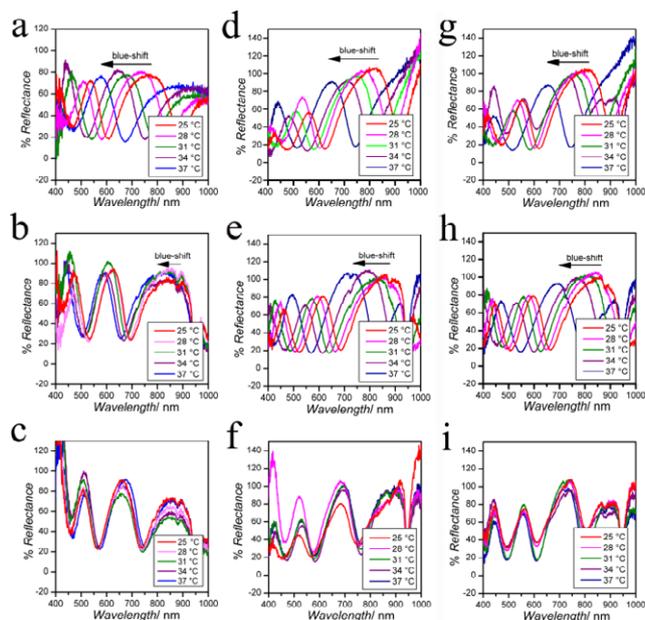
Materials: *N*-isopropylacrylamide was purchased from TCI (Portland, Oregon) and purified by recrystallization from hexane (98.5 +%, Sigma-Aldrich) before use. *N,N'*-methylenebisacrylamide (BIS) (99%), acrylic acid (AAc) (99%) and ammonium persulfate (APS) (98 +%) were obtained from Sigma-Aldrich (Oakville, Ontario). Hydrochloric acid was obtained from Caledon Laboratories Ltd. Sodium chloride, sodium hydroxide and glass substrates (25mm × 25mm) were purchased from Fisher (Ottawa, Ontario). Deionized water was filtered to have a resistivity of 18.2 MΩ and was produced by a Milli-Q Plus system (Millipore Co.). Cr (99.999%) was purchased from ESPI Company, while Au (99.99%) was purchased from MRCs Canada (Edmonton).

Microgel Synthesis: Microgels (“medium” size) and etalons were prepared as previously described.¹⁹ Photographs were taken using a Nikon camera equipped with a 40 mm Nikon macrolens. The various pH solutions were made to have an ionic strength of 2 mM, by adjustment with NaCl. The microgel diameter was measured using a ALV/CGS-3 compact goniometer (Germany) with a HeNe laser (incident beam = 632.8 nm, scattering angle = 90°). All measurements were taken at 25 °C in pH 3 solution (2 mM ionic strength). Each hydrodynamic diameter was reported as an average of 30 s acquisitions and averaged over five measurements.

Etalon Fabrication: Microgel based etalons were fabricated as previously described.^{8, 18-20} Briefly, 2 nm Cr and 15 nm of Au was added to a 25 x 25 mm ethanol rinsed and N₂ gas dried glass coverslip at a rate of 1 Å s⁻¹, and 0.1 Å s⁻¹, respectively, using a Torr International Inc. (New Windsor, NY) thermal evaporation system Model THEUPG. The Au coated substrates were annealed at 250°C for 3 h using a Thermolyne muffle furnace from Thermo Fisher Scientific (Ottawa, Ontario). An annealed Au coated glass substrate was rinsed with EtOH and dried with N₂ and was placed onto hot plate set to 30 °C along with the tube containing a concentrated microgel pellet (from centrifugation). A 40 μL aliquot of the concentrated microgels was added to the Au substrate, and spread out to cover the whole substrate until the layer was unspreadable (close to drying). The microgels were allowed to completely dry at 35 °C for 2 h. The film was rinsed copiously with deionized water and soaked overnight in water at ~30 °C. Following soaking, the substrates were again rinsed with DI water and dried with N₂ gas and another Cr/Au layer (2 nm Cr, 15 nm Au) was added to the microgel layer. The etalons were then soaked in DI water overnight at 30 °C and dried with N₂ gas prior to use.

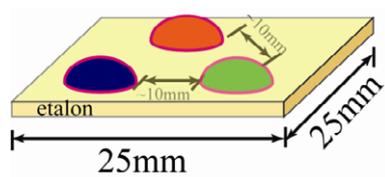
Transparency slides (Canon Inc., Lake Success, NY) were cut to an approximate dimension of 25 mm x 80 mm. The cut pieces were affixed to a microscope slide with tape, and 2 nm Cr and 15 nm of Au were evaporated onto the substrate as above. These transparencies were treated in the same manner as glass substrates to yield etalons.

Reflectance Spectroscopy: Reflectance spectra were collected by a Red Tide USB650 spectrometer, connecting with a LS-1 tungsten light source and a reflectance probe (Ocean Optics, Dunedin). In a typical process, a Corning PC-420D hot plate (Fisher, Ottawa, Ontario) was used to control temperatures; at the meantime, the temperature was also monitored with a thermometer (thermocouple platinum sensor). The spectra were collected over a wavelength range of 400-1000 nm and analyzed by Ocean Optics Spectra Suite Spectroscopy software (integration time: 100 milliseconds, scans to average: 2).



SI Figure 1. Reflectance spectra for different etalons obtained for the spots at different pHs as a function of temperatures (pH 3.0: a, d, g; pH 4.0: b, e, h; pH 7.0 c, f, i).

Scheme S1



The spatial location of individual spots with different pH in our experiment.