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CO_2-Switchable Poly (*N*-Isopropylacrylamide) Microgel-Based Etalons

Qiang Matthew Zhang, Andrews Ahiabu, Yongfeng Gao, Michael J. Serpe*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

E-mail: michael.serpe@ualberta.ca; Fax: +1 780 492 8231; Tel: +1 780 492 5778.

Experimental Details.

TEM images were obtained on an ultrahigh-resolution transmission electron microscope (JEOLJEM-2010FEF) using an accelerating voltage of 200 kV. DLS measurements were carried out by using a DLS/SLS-5000 compact goniometer (ALV, Langen) coupled with an ALV photon correlator.

Microgel synthesis.

A 3-necked round bottom flask was fitted with a reflux condenser, nitrogen inlet, and temperature probe, and charged with a solution of N-isopropylacrylamide (11.9 mmol), a certain amount of 4-vinyl pyridine (depending on the specific concentration desired), and BIS (0.6 mmol) in 99 mL deionized water, previously filtered through a 0.2 mm filter. The solution was purged with N_2 and allowed to heat to 70 °C over ~1 hour. The reaction was then initiated with a solution of ammonium persulfate (0.2 mmol) in 1 mL of deionized water. The reaction proceeded at 70 °C for 4 hours under a blanket of nitrogen. The resulting suspension was allowed to cool overnight while stirring, and then it was filtered through a Whatman #1 paper filter to remove any large aggregates. The microgel solution was then distributed into centrifuge tubes and purified via centrifugation at ~8300 rcf to form a pellet, followed by removal of the supernatant and resuspension with deionized water, 6 times. The cleaned microgels were recombined and stored in a brown glass jar.

Preparation of etalons

To fabricate the Au coated coverslips (etalon underlayer), 2 nm Cr and 15 nm of Au was added to a 25 x 25 mm ethanol rinsed and N_2 gas dried glass coverslip (Fisher's Finest, Ottawa, ON) at

a rate of 1 Å s^{-1}, and 0.1 Å s^{-1}, respectively (Torr International Inc., thermal evaporation system, Model THEUPG, New Windsor, NY). The Cr/Au substrates were annealed at 250 °C for 3 h (Thermolyne muffle furnace, Ottawa, ON) and cooled to room temperature prior to microgel film deposition.

Approximately 5-10 mL of microgel solution was centrifuged at ~8300 rcf to form a pellet. The supernatant was removed and discarded, and the pellet was vortexed to loosen and homogenize the particles in the remaining solvent. A 40 µL aliquot of concentrated microgels was spread onto an annealed 25 mm x 25 mm Au-coated glass coverslip. The film was allowed to dry on a 30 °C hotplate for 30 minutes before the excess microgels not bound directly to the Au layer were rinsed away with deionized water. The samples were then soaked overnight at 30 °C in a deionized water bath. The samples were then rinsed with deionized water, dried with N_2, and another Au overlayer (2 nm Cr for adhesion, followed by 15 nm Au) was added. The completed device was soaked overnight in deionized water at 30 °C before spectral analysis.

Reflectance spectroscopy

Reflectance measurements were conducted in a specially designed sample holder using a USB2000+ spectrophotometer, a HL-2000-FHSA tungsten light source, and a R400-7-VISNIR optical fiber reflectance probe, all from Ocean Optics (Dunedin, FL). The spectra were recorded using Ocean Optics Spectra Suite Spectroscopy Software over a wavelength range of 350–1,025 nm. Measurements were performed in the sample holder, which allows for careful sample positioning, sample stability, and fine temperature control. Dry ice was used as the CO_2 gas source, and CO_2 gas was bubbled into solution during the test process. The light source was always positioned over the center of the etalon.

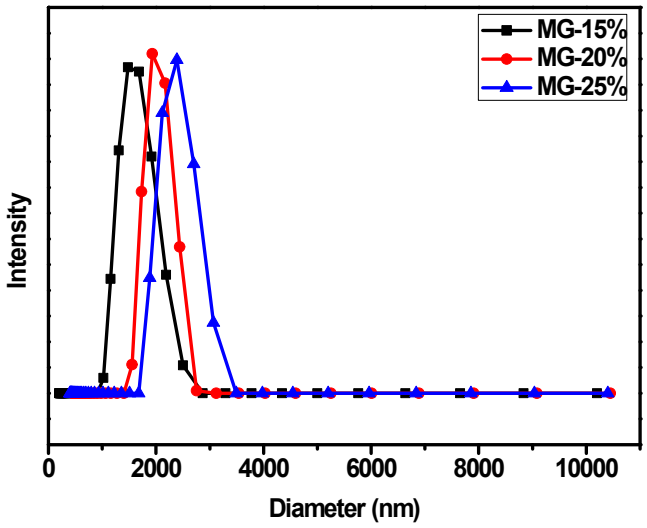

Figure S1. Microgel diameter at 30 ^{o}C determined by dynamic light scattering (DLS).

(a) (b)

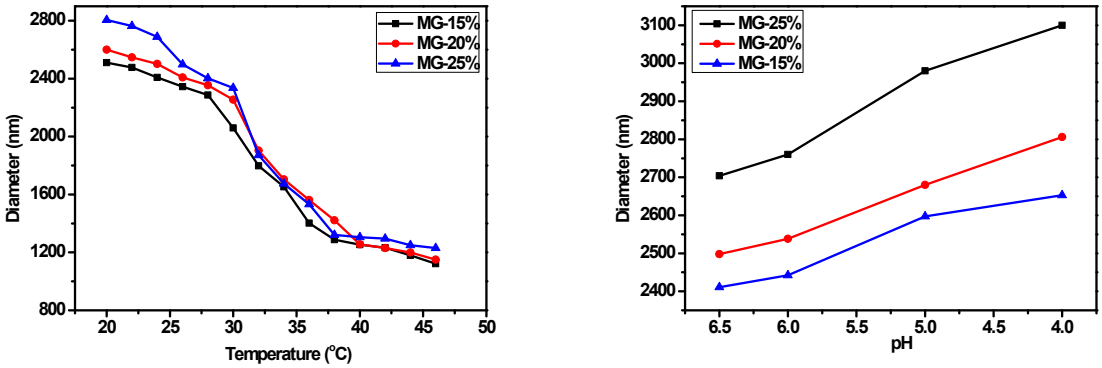

Figure S2. (a) DLS measured microgel diameters at pH = 6.5 as a function of temperature; (b) DLS measured microgel diameters as a function of pH at 22 °C.

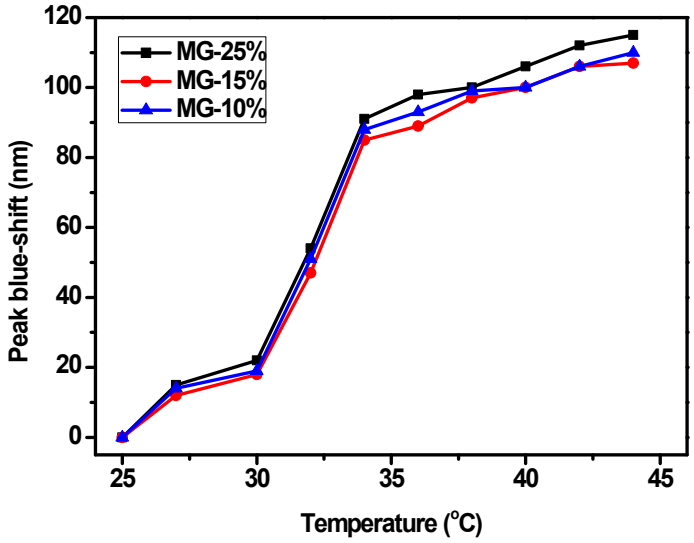

Figure S3. λ_5 peak blue-shift for the indicated microgel-based etalons as a function of temperature. Peak blue-shift was calculated by λ_5 (T) - λ_5 (25 °C).

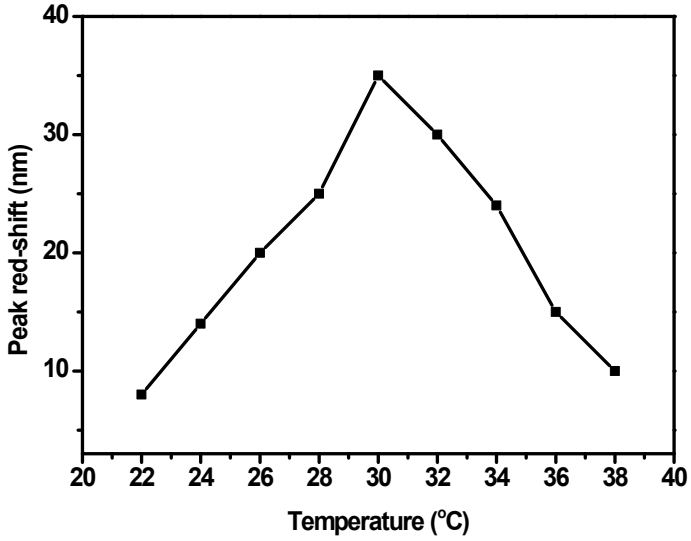

Figure S4. λ_5 peak red-shift of MG-25% etalon as a function of temperature after exposure to CO_2. Peak red-shift was calculated by λ_5 (after exposure to CO_2) - λ_5 (before exposure to CO_2).

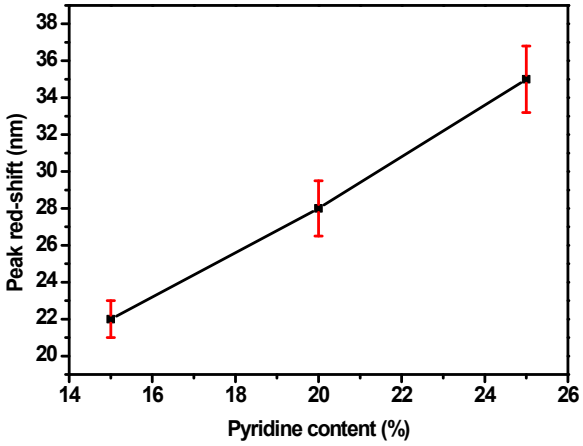

Figure S5. λ_5 peak red-shift as a function of pyridine content after exposure to CO_2. Peak red-shift was calculated by λ_5 (after exposure to CO_2) - λ_5 (before exposure to CO_2).

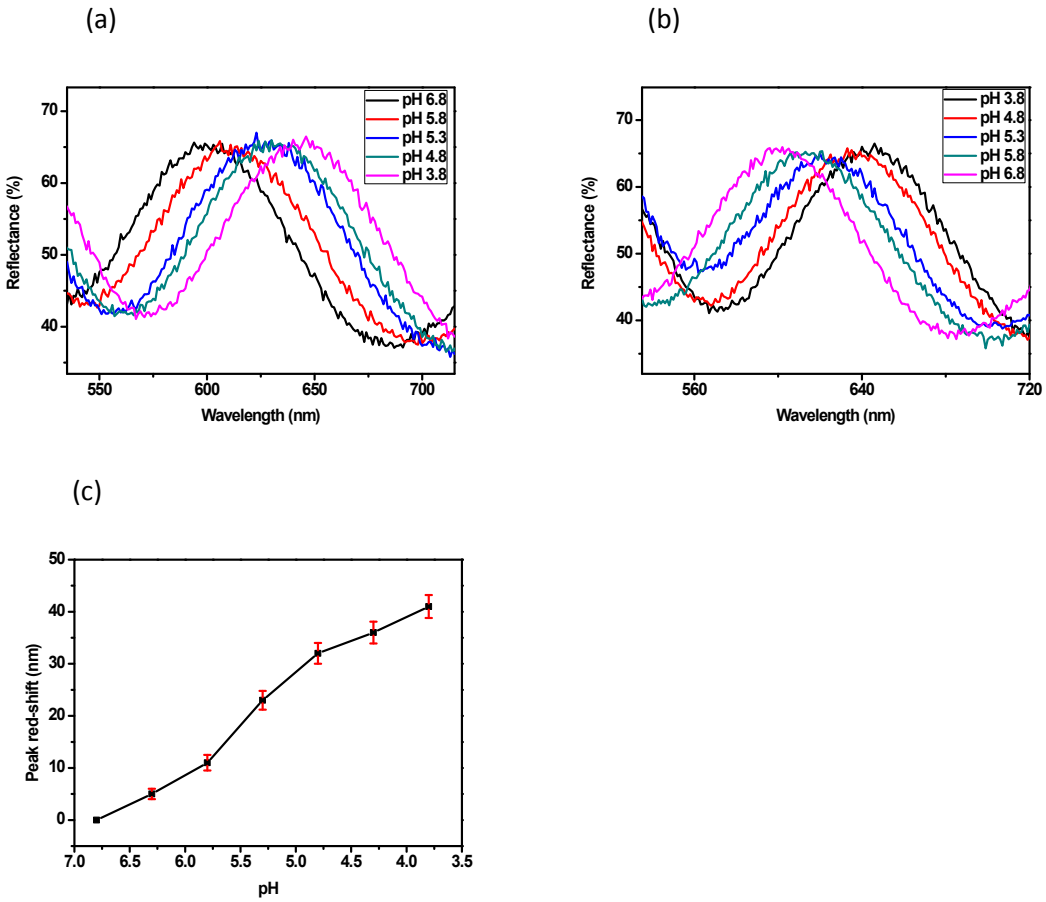

Figure S6. (a) Reflectance spectra (λ_5) for a MG-25% etalon with pH from 6.8 to 3.8; (b) Reflectance spectra (λ_5) for a MG-25% etalon with pH from 3.8 to 6.8 at 30 ^{o}C; (c) λ_5 peak red-shift of MG-25% as a function of pH at 30 ^{o}C, it was calculated by λ_5 (pH) - λ_5 (pH = 6.8).

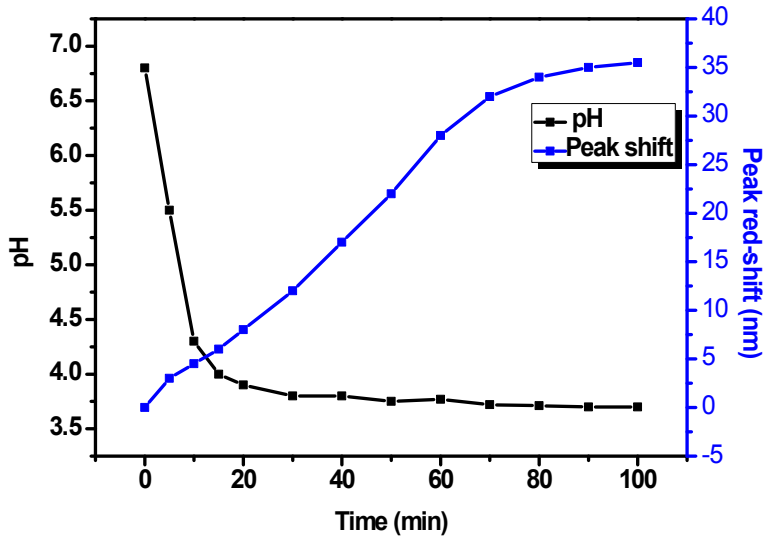

Figure S7. λ_5 Peak red-shift and pH of MG-25% etalon as a function of time after exposure to CO_2 at 30 ^oC, it was calculated by λ_5 (time) - λ_5 (time = 0).