

# A “Paint-On” Protocol for the Facile Assembly of Uniform Microgel Coatings for Color Tunable Etalon Fabrication

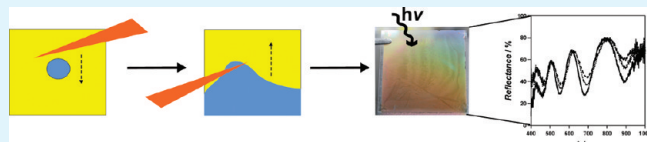
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Supporting Information

**ABSTRACT:** Robust, uniform, monolithic microgel thin films can be created by actively spreading a concentrated solution of microgels onto a Au surface at 30 °C. The method is easy, fast, and seemingly universal: it can be used to coat a variety of Au coated surfaces with microgels containing different chemical functionalities. No control of the deposition conditions, other than temperature and microgel concentration, is required. We show that this technique consistently produces monolithic microgel films on Au-coated surfaces, and it has been extended to coat Si substrates. After deposition of a thin Au overlayer onto the deposited microgel layer, the materials are colored, as evidenced by multiple peaks in their reflectance spectra. The assemblies deposited using the described “paint-on” technique show increased spectral and visual purity over the entire surface area as compared to colored materials made by a previously used passive drying process.

**KEYWORDS:** pNIPAm microgels, polymer thin films, stimuli responsive materials, metal–polymer hybrid structures



## INTRODUCTION

Optical materials are of particular interest for sensors,<sup>1,2</sup> coatings,<sup>3</sup> and filters.<sup>4</sup> They are often composed of ordered materials of contrasting refractive indices, which interact with incident light to produce color.<sup>1,2,5,6</sup> Responsive microgels are colloidally stable hydrogel spheres that undergo a change in response to a stimulus. Ideally, this response is reversible. Among the most well studied responsive microgels are those composed of poly(*N*-isopropylacrylamide) (pNIPAm). pNIPAm-based microgels can be synthesized on the order of 50 nm to 1.5 μm in diameter,<sup>7–10</sup> and are thermoresponsive. These thermoresponsive microgels expel their water of solvation by deswelling (diameter decrease) above ~31–32 °C and reswell (diameter increase) when cooled below that temperature.<sup>7,11</sup> With copolymerization, chemical functionality and added responsivity can be incorporated into the microgels. Acrylic acid (AAc), for instance, renders the microgels pH responsive, and adds a chemical handle to which other functionality can subsequently be attached.<sup>12,13</sup> These microgels, then, are truly multiresponsive: a property that we exploit to make color tunable optical materials.<sup>14</sup> The responsiveness of pNIPAm-based microgels can be used to affect a multitude of material properties and functions, the most important here being the ability to tune lattice spacing in ordered materials, which results in a concomitant color change.<sup>14</sup>

Microgels can be deposited on surfaces such as glass, plastics, gold, and silicon by a variety of methods.<sup>6,15–21</sup> Often, microgels retain the same properties they exhibit in solution when dried on a solid substrate.<sup>6</sup> Drying from aqueous solution,<sup>6,20</sup> dip coating,<sup>21</sup> spin coating,<sup>15,19</sup> adsorption,<sup>16,18</sup> and centrifugation<sup>17</sup> can all be employed to fabricate thin films of microgels with varying intermicrogel distances depending on the method and conditions used. However, these techniques can be time-consuming, and

they often yield inhomogeneous and/or sparse microgel coverage. In certain circumstances, such as drug delivery,<sup>22,23</sup> medical device coatings,<sup>24</sup> solar cells,<sup>25</sup> and batteries,<sup>26</sup> it is desirable to generate dense, closely packed microgel films and conformal, monolithic polymer coatings. For example, we recently reported on color tunable microgel-based etalons.<sup>14</sup> A Fabry–Pérot interferometer, or etalon, is an optical device composed of two planar mirrors separated by a dielectric layer.<sup>27</sup> This device interacts with light, via interference, to reflect/transmit specific wavelengths of light. The wavelengths can be varied by changing the mirror–mirror distance, the refractive index of the dielectric layer, the angle of incident light and/or the angle of observation. Etalons fabricated as part of our studies are composed of two Au mirrors, separated by a layer of pNIPAm-co-AAc microgels. We showed that when the assemblies were immersed in water they exhibited color (observed visually and spectrally), which could be tuned by temperature and pH.<sup>14</sup> The color tunability was attributed to the direct modulation of the mirror–mirror spacing because of the size change of the microgels with temperature; changes in refractive index with microgel deswelling were determined to be negligible compared to the change in mirror spacing. We are developing these materials for fundamental studies of the nature of pNIPAm-co-AAc microgel responsivity after immobilization on surfaces and at interfaces. For example, the new materials will allow us to directly probe the kinetics of deswelling of microgel thin films, and determine the exact solvation state of the microgels as a function of temperature and pH. Although we are interested in these more fundamental aspects of microgels, we are also interested in using these materials for various applications. These

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materials could be used for light filtering applications,<sup>28</sup> chem/biosensing,<sup>29</sup> controlled small molecule release (drug delivery),<sup>30</sup> and as polymer/inorganic responsive surfaces.<sup>31</sup>

To achieve the goals set above, spectrally and visually pure etalons need to be constructed over the complete surface area on which they are generated. The materials should have a uniform color and the reflectance spectrum should not vary significantly with the location we are probing. Since the color of the materials is a direct result of the mirror–mirror spacing, it is directly affected by the quality of the microgel layer between the mirrors. We define quality in terms of the immobilized microgel density and the uniformity of the coverage: dense, uniformly coated, or “jammed” microgel layers yield visually and spectrally pure etalons. In fact, the microgels in these “jammed” layers are so closely packed that the microgel structure is no longer easily distinguishable, and the microgels in the film form a monolithic polymer layer that completely coats the substrate with virtually no holes (defects). It should also be pointed out that although monolithic microgel layers are needed to fabricate microgel etalons, we believe this to be a general protocol to coat a multitude of Au coated substrates with uniform, dense microgel coatings. As Au can easily be added to a variety of substrates, this can be a universal coating procedure. Additionally, we imagine that these microgel layers can be deposited on surfaces coated with other metals, e.g., Ti, Ag, and this will be the topic of future studies.

In this submission, we demonstrate that microgels with a variety of chemical functionalities can be painted on Au coated substrates to yield dense polymer coatings, further expanding the utility of the method. It appears that microgel functionality does not affect the quality of the resulting film. The coatings also appear to be extremely robust, and we demonstrate that the technique can be applied to Au coated glass, plastic, and clean Si substrates.

## EXPERIMENTAL DETAILS

**Materials.** *N*-Isopropylacrylamide was purchased from TCI (Portland, Oregon) and purified by recrystallization from hexanes (ACS reagent grade, EMD, Gibbstown, NJ) prior to use. *N,N'*-methylenebisacrylamide (BIS) (99%), acrylic acid (AAc) (99%), 3-butenic acid (vinylacetic acid, VAA) (97%), acrylamide (AAM) ( $\geq 99\%$ ), formic acid (50% in water), and ammonium persulfate (APS) (98+%) were obtained from Sigma-Aldrich (Oakville, Ontario) and were used as received. Various salts used for buffer solutions and for adjusting ionic strength were obtained from EMD and were used as received. All deionized (DI) water was filtered to have a resistivity of 18.2 M $\Omega$ ·cm and was obtained from a Milli-Q Plus system from Millipore (Billerica, MA). Au annealing was performed in a Thermolyne muffle furnace from Thermo Fisher Scientific (Ottawa, Ontario). Anhydrous ethanol was obtained from Commercial Alcohols (Brampton, Ontario). Hydrochloric acid was purchased from Caledon Chemicals (Georgetown, Ontario). Fisher's Finest glass coverslips were 25 mm  $\times$  25 mm and obtained from Fisher Scientific (Ottawa, Ontario). Transparencies were from Canon Inc. (Lake Success, NY). Silicon wafers (1–0–0, *N*-type, 0.5 mm thick) were obtained from University Wafer (Boston, MA). Cr and Au were 99.999% and obtained from ESPI (Ashland, OR). Photographs of the films were taken with an Olympus C-7070 Wide Zoom or a Pentax K2000 DSLR camera fitted with a SMC Pentax-DA 1:2.8 35 mm rectilinear macro lens.

**Microgel Synthesis.** Microgels composed of poly (*N*-isopropylacrylamide-*co*-acrylic acid) (pNIPAm-*co*-AAc-1) were synthesized via temperature-ramp, surfactant free, free radical precipitation polymerization as described previously.<sup>9</sup> The monomer mixture was comprised of 85% *N*-isopropylacrylamide (NIPAm) and 10% acrylic acid (AAc) with

5% *N,N'*-methylenebisacrylamide (BIS) cross-linker (154 mM total monomer concentration). The monomer, NIPAm (8.5 mmol), and the cross-linker, BIS (0.51 mmol), were dissolved in deionized water (50 mL) with stirring in a small beaker. The mixture was filtered through a 0.2  $\mu$ m filter affixed to a 20 mL syringe into a 100 mL, 3-neck round-bottom flask. An additional aliquot of deionized water (12.5 mL) was used to wash the beaker, which was filtered and transferred to the round-bottom flask. The flask was then fitted with a temperature probe, a condenser/N<sub>2</sub> outlet, stir bar, and a N<sub>2</sub> inlet. The monomer solution (62.5 mL total volume) was purged with N<sub>2</sub> gas for  $\sim$ 1 h, with stirring at a rate of 450 rpm, while the temperature was allowed to reach 45 °C. AAc (1.0 mmol) was added to the heated mixture with a micropipet. A 0.078 M aqueous solution of APS (2.5 mL) was delivered to the monomer solution with a transfer pipet to initiate the reaction (total reaction volume 65.0 mL). Immediately following initiation, a temperature ramp of 45–65 °C was applied to the solution at a rate of 30 °C/h. Following completion of the ramp, the reaction was allowed to proceed overnight at 65 °C. After polymerization, the reaction mixture was filtered through glass wool to remove any large aggregates. The coagulum was rinsed with deionized water and the reaction solution was diluted to  $\sim$ 120 mL (diluted approximately 2 $\times$  from the original microgel solution concentration). An aliquot of these microgels (12 mL) was centrifuged at a speed of  $\sim$ 8400 relative centrifugal force (rcf) at 23 °C, to produce a pellet at the bottom of the centrifuge tube. The supernatant was removed from the pellet of microgels, which were then resuspended to their original volume (12 mL) using deionized water. This process was completed a total of four times to remove unreacted monomer and linear polymer from the microgels.

Microgels were also synthesized using other previously described techniques<sup>15,32</sup> without a comonomer (pNIPAm-BIS microgels, 5% cross-linker), as well as with vinylacetic acid (pNIPAm-*co*-VAA, 10 mol %) and acrylamide (pNIPAm-*co*-AAM, 10 mol %) comonomers. Medium<sup>15</sup> (pNIPAm-*co*-AAc-2) and small<sup>32</sup> (pNIPAm-*co*-AAc-3) diameter acrylic acid (10 mol %) microgels were also synthesized. Cross-linker concentration for all syntheses was 5 mol % and the NIPAm amount was adjusted accordingly to accommodate the respective comonomer.

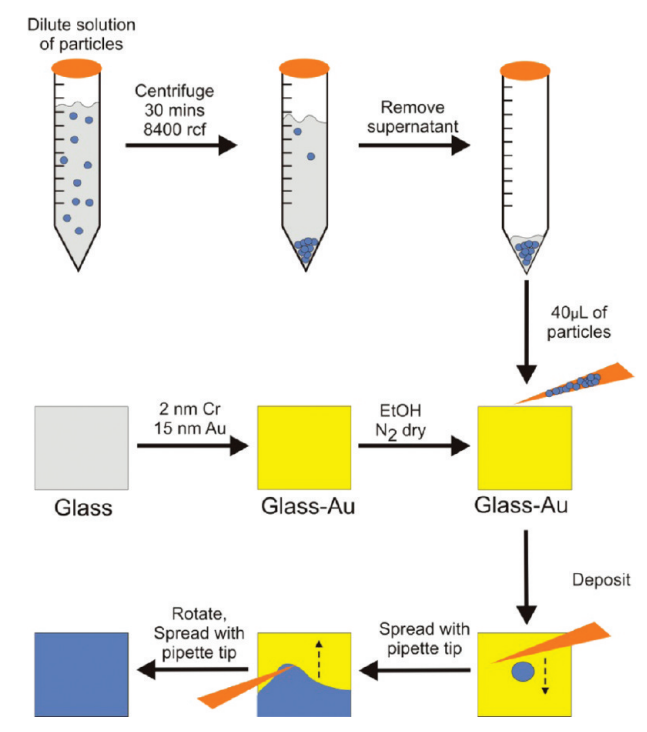
**Substrate Fabrication.** To fabricate the Au-coated coverslips (etalon underlayer), we added 2 nm Cr and 15 nm of Au to a 25 mm  $\times$  25 mm ethanol rinsed and N<sub>2</sub> gas dried glass coverslip at a rate of 1  $\text{\AA}$  s<sup>-1</sup>, and 0.1  $\text{\AA}$  s<sup>-1</sup>, respectively, using a Torr International Inc. (New Windsor, NY) thermal evaporation system Model THEUPG. The Cr/Au films were annealed at 250 °C for 3 h and cooled to room temperature prior to microgel solution deposition.

Transparency slides were cut to an approximate dimension of 25 mm  $\times$  80 mm, rinsed with ethanol and dried with N<sub>2</sub>. 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.

Silicon wafers were cut to an approximate dimension of 25 mm  $\times$  25 mm and cleaned with piranha solution (75:25 H<sub>2</sub>SO<sub>4</sub>: H<sub>2</sub>O<sub>2</sub>) for 30 min. The cleaned substrates were rinsed copiously with water and dried with N<sub>2</sub> prior to Au coating.

**“Paint-on” Technique.** For most syntheses, an aliquot of a given microgel solution (above) was centrifuged for 30 min at 23 °C at  $\sim$ 8400 relative centrifugal force (rcf) in order to pack the microgels into a concentrated pellet. Microgels with a small diameter were centrifuged at 29 °C for 2 h at  $\sim$ 8400 rcf. The supernatant was removed. An annealed 25 mm  $\times$  25 mm Au coated glass substrate was rinsed with EtOH and dried with N<sub>2</sub> and was placed onto hot plate set to 30 °C along with the tube containing the microgel pellet, for about 5 min. A 40  $\mu$ L aliquot of the concentrated microgels was deposited onto the Au substrate, and spread toward each edge using the side of a micropipet tip, taking care not to scratch the Au substrate. The film was rotated 90° and the microgel solution was spread again. The spreading and rotation continued as the microgel layer dried. To avoid having the microgels stick to

### Scheme 1. Cartoon Illustrating the Described “Paint-On” Method



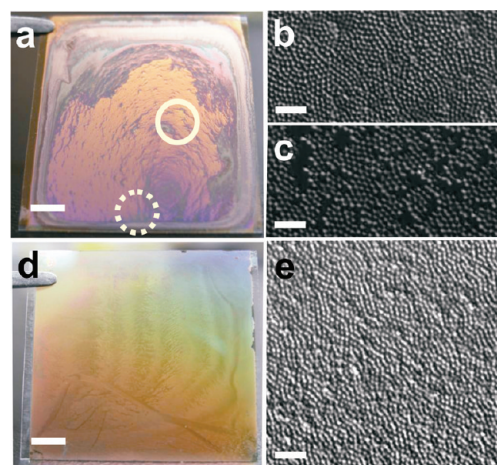
the tip of the pipet — compromising the microgel film quality — the spreading ceased when the layer became noticeably viscous (Scheme 1). The microgels were allowed to dry completely by increasing the hot plate temperature to 35 °C and allowing the film to dry at that temperature for 2 h. The film was rinsed copiously with deionized water to remove any excess microgels. The film was then placed into a deionized water bath and allowed to sit overnight at ~30 °C.

The same protocol was used for the silicon substrates. It was also used to coat the Au coated transparency slide, with the exception that the quantity of concentrated microgels was increased to 80  $\mu\text{L}$  to cover the larger substrate, which was not annealed prior to coating.

**Etalon Fabrication.** Films were made from the cleaned microgels using the above “paint-on” method. Following film drying and overnight soaking, the slides were rinsed with DI water and dried with  $\text{N}_2$  gas. The film was placed into the metal evaporator and a Cr/Au layer (2 nm Cr, 15 nm Au) was added as an overlayer as previously described.<sup>14</sup> Prior to any measurements, the etalons were soaked in DI water overnight at 30 °C. This was necessary to allow the microgel layer between the Au layers to solvate completely.

**Reflectance Spectroscopy.** Reflectance measurements were conducted using a Red Tide USB650 spectrometer, a LS-1 tungsten light source, and a reflectance probe from Ocean Optics (Dunedin, FL). The spectra were recorded using Ocean Optics Spectra Suite Spectroscopy Software at room temperature over a wavelength range of 400–1000 nm. Measurements were conducted by placing the film in a Petri dish with water at room temperature. The probe tip was immersed in the water and its distance from the etalon surface adjusted for optimal signal. The probe remained undisturbed between measurements to ensure that all of the spectra were taken in the same manner. The film was moved under the probe and at least three measurements were taken for each film in different areas.

**Optical Microscopy.** Microscope images of the films were taken using an Olympus IX71 inverted microscope (Markham, Ontario) fitted



**Figure 1.** Photographs and DIC microscopy images showing microgel films fabricated from the two methods described. (a) The photograph of an etalon made by our previously used drying method, and the corresponding DIC microscopy images of (b) an area that is an etalon, and (c) an area that is not an etalon. The microscopy images were taken before Au coating in regions approximated by the white circles in a. The solid white circle corresponds with b, and the dashed white circle corresponds with c. (d) Photograph of an etalon made by the presented “paint-on” method, and (e) the corresponding DIC microscopy image before Au coating to make the etalon in d. The microgel coverage was uniform across the whole surface area of the substrate. The photographs were taken with an Olympus C-7070 Wide Zoom digital camera, after the addition of a 2 nm Cr and 15 nm Au layer on top of the microgels as an overlayer. DIC microscopy images were obtained before Au overlayer addition with a 100 $\times$  oil immersion objective. Scale bars are 5 mm for the photographs, and 5  $\mu\text{m}$  for the micrographs.

with a 100 $\times$  oil-immersion objective, and a 10 $\times$  eyepiece, differential interference contrast (DIC) optics, and a Andor Technology iXon+ camera (Belfast, Ireland). A 1.6 $\times$  magnification booster was used where specified. Andor SOLIS v4.15.3000.0 software was used to record microscope images of the microgel films. An image of an Edmunds Industrial Optics (Barrington, NJ) PYSER-SGI scale grating (50  $\mu\text{m}$   $\times$  2  $\mu\text{m}$ ) was used to determine the scale bars.

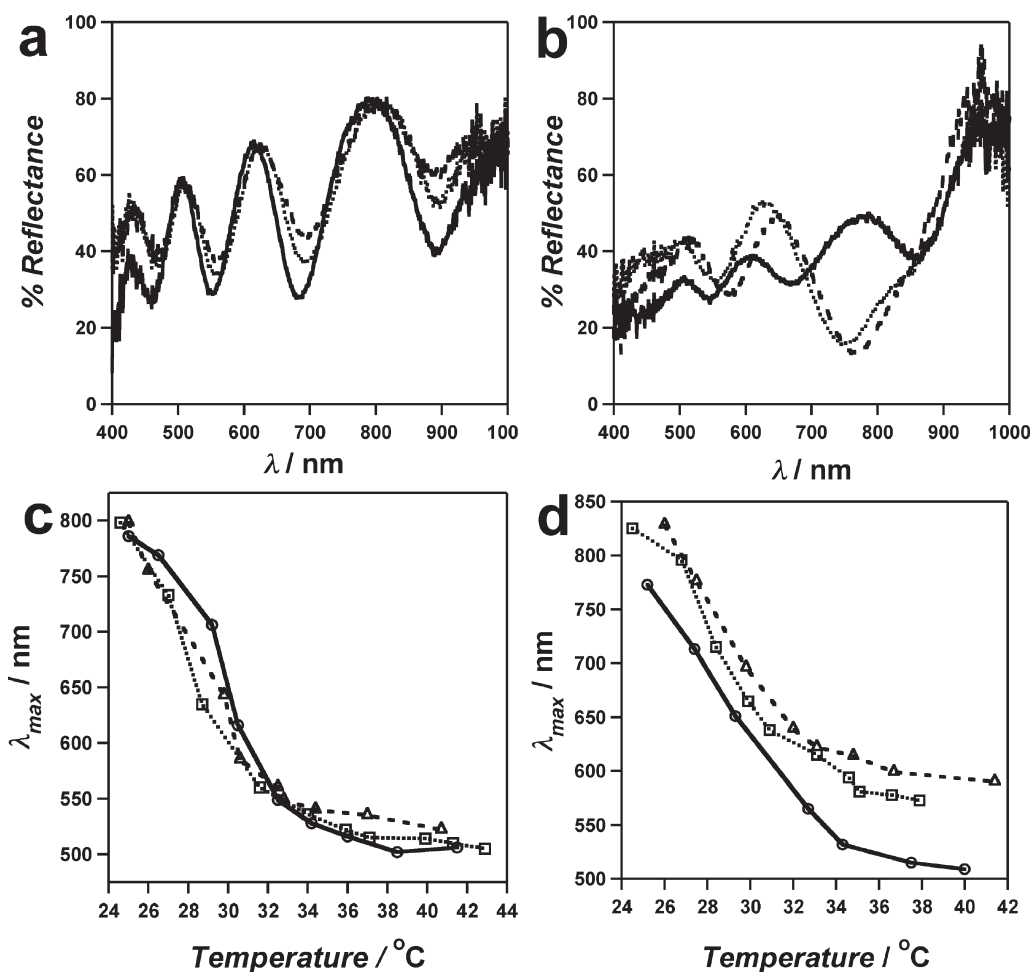
**Scanning Electron Microscopy.** Images of the microgel films were taken with a LEO 1430 SEM (Carl Zeiss SMT AG, formerly LEO Electron Microscopy Ltd., Oberkochen, Germany). Samples in the SEM were tilted 80° relative to the source.

**Photon Correlation Spectroscopy (PCS).** PCS measurements were performed using a Brookhaven Instruments ZetaPlus zeta potential analyzer and ZetaPlus microgel sizing software v.5 (Holtville, NY). All measurements were taken at 25 °C in 10 mM formate buffer (pH 3.0, 10 mM ionic strength as NaCl). Each hydrodynamic diameter is reported as an average of five 30 s acquisitions and averaged over five measurements per sample.

## RESULTS AND DISCUSSION

In our previous studies,<sup>14</sup> etalons were made by allowing 775  $\mu\text{L}$  of a 5% (v/v) solution of ~1.5  $\mu\text{m}$  diameter pNIPAm-co-AAc-1 microgels to air-dry on a Au coated glass coverslip (2 nm Cr was used as an adhesion layer followed by 15 nm Au). Figure 1a shows a photograph of the resultant film after coating with a 2 nm Cr/15 nm Au overlayer to make the etalon. Figure 1 (b,c) show differential interference microscopy (DIC) images of the resultant microgel film in Figure 1 (a), prior to the Cr/Au overlayer addition. As can be seen, the film’s color is visually variable, and the microgel packing density is not consistent from





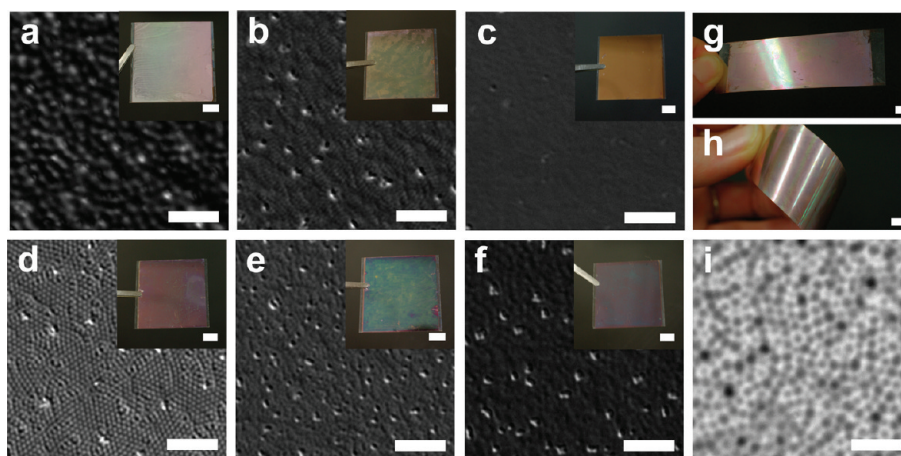
**Figure 2.** Reflectance spectra for three randomly selected regions of etalons made by (a) the “paint-on” method, and (b) the overnight drying method. The phase transition of the etalons obtained by plotting  $\lambda_{\max}$  for one peak in the spectrum as a function of temperature for etalons made by (c) the “paint-on” method, and (d) the overnight drying method. The graphs represent randomly selected regions, region 1 (solid), region 2 (dotted), and region 3 (long dashes). Note that in b and d, a fourth randomly selected region was not an etalon and is not plotted. All data were collected for the etalons in pH 3 water (I.S. = 1).

location to location. Additionally, we determined that it was not possible to completely coat a Au substrate with a dense, monolithic layer of microgels by simply increasing the microgel concentration, and air-drying (over the concentration range investigated). These effects are most likely a result of the so-called “coffee-ring effect”.<sup>33,34</sup> Microgels appear concentrated in certain regions of the film, caused by the presence of high capillary flow at drying boundaries. The flow carries and deposits a higher concentration of the microgels to the edge of the drying droplet. As the droplet evaporates, an oscillating pinning/dewetting process<sup>35,36</sup> takes place at the drying edge, while microgels are simultaneously adhering to the surface in the bulk droplet itself. It is the combination of the coffee ring effect and the native attraction of the microgels to the surface in the bulk droplet that is most likely resulting in the observed inconsistent surface coverage.

On the basis of the efforts of many groups to understand and manipulate the assembly of colloids onto surfaces from dilute solution,<sup>33–35,37–39</sup> we hypothesized that modifying the properties of the deposition solution would affect the resultant film structure. Microgel concentration, drying time, surfactant concentration, cosolvent ratios, and pH and ionic strength were all

investigated (see the Supporting Information). Although the different deposition conditions did yield films with slightly improved surface coverage, no combination of the above solution conditions resulted in the desired jammed microgel layers. However, from the experiments, it was confirmed that drying is critical for making jammed microgel films, i.e., exposing a Au-coated surface to a microgel solution for increasing time (without drying) does not result in increased surface coverage. Only by drying can one manipulate the surface coverage. Therefore, we reasoned that to counteract the coffee-ring effect, microgels needed to be highly concentrated and the drying process needed to be continuously disrupted.

To achieve this, we developed the “paint-on” method as detailed in the experimental, and shown in Scheme 1. Briefly, microgels concentrated by centrifugation were spread onto an annealed, clean, Au coated glass substrate and allowed to dry completely. Once completely dry, the film was rinsed copiously with deionized water to remove any microgels that were not directly bound to the Au substrate. The film was then placed into a deionized water bath and allowed to sit overnight at  $\sim 30$  °C. Soaking the film in this manner increases the quality of the resultant etalon, likely a result of possible multilayers breaking up



**Figure 3.** DIC microscopy images and photographs (insets) showing films made from (a) pNIPAm-co-AAC-1 microgels, (b) pNIPAm-co-AAC-2 microgels, (c) pNIPAm-co-AAC-3 microgels, (d) pNIPAm-BIS microgels, (e) pNIPAm-co-AAm microgels, (f) pNIPAm-co-VAA microgels. Photographs of an etalon generated from pNIPAm-co-AAC-1 microgels deposited on a flexible surface, (g) unbent and (h) bent, and (i) a DIC micrograph of the microgel film on the flexible substrate. Scale bars are 5  $\mu\text{m}$  and 5 mm for the micrographs and photographs, respectively. All DIC images were taken before the addition of the Cr/Au overlayer; all photographs were taken after the addition of a Au overlayer using a Pentax K-2000 DSLR camera. The DIC image shown in (i) was taken through a glass coverslip with the sample inverted on top in order to match the optical path required for the objective. All DIC images except (d) were taken using a 1.6 $\times$  magnification booster. The defects seen in panels (b), (d), (e), and (f) are features on the Cr/Au underlayer and we hypothesize that they formed during the Au evaporation and/or annealing processes. These features do not impact the optical properties or quality of etalons made via this technique (as seen in Figure 4).

**Table 1. Hydrodynamic Radii and the Standard Deviations for the Microgels Investigated**

microgel	hydrodynamic diameter, $D_H$ (nm)
pNIPAm-co-AAC-1	1548 $\pm$ 69
pNIPAm-co-AAC-2	659 $\pm$ 21
pNIPAm-co-AAC-3	229 $\pm$ 10
pNIPAm-BIS	671 $\pm$ 17
pNIPAm-co-AAm	653 $\pm$ 10
pNIPAm-co-VAA	602 $\pm$ 17

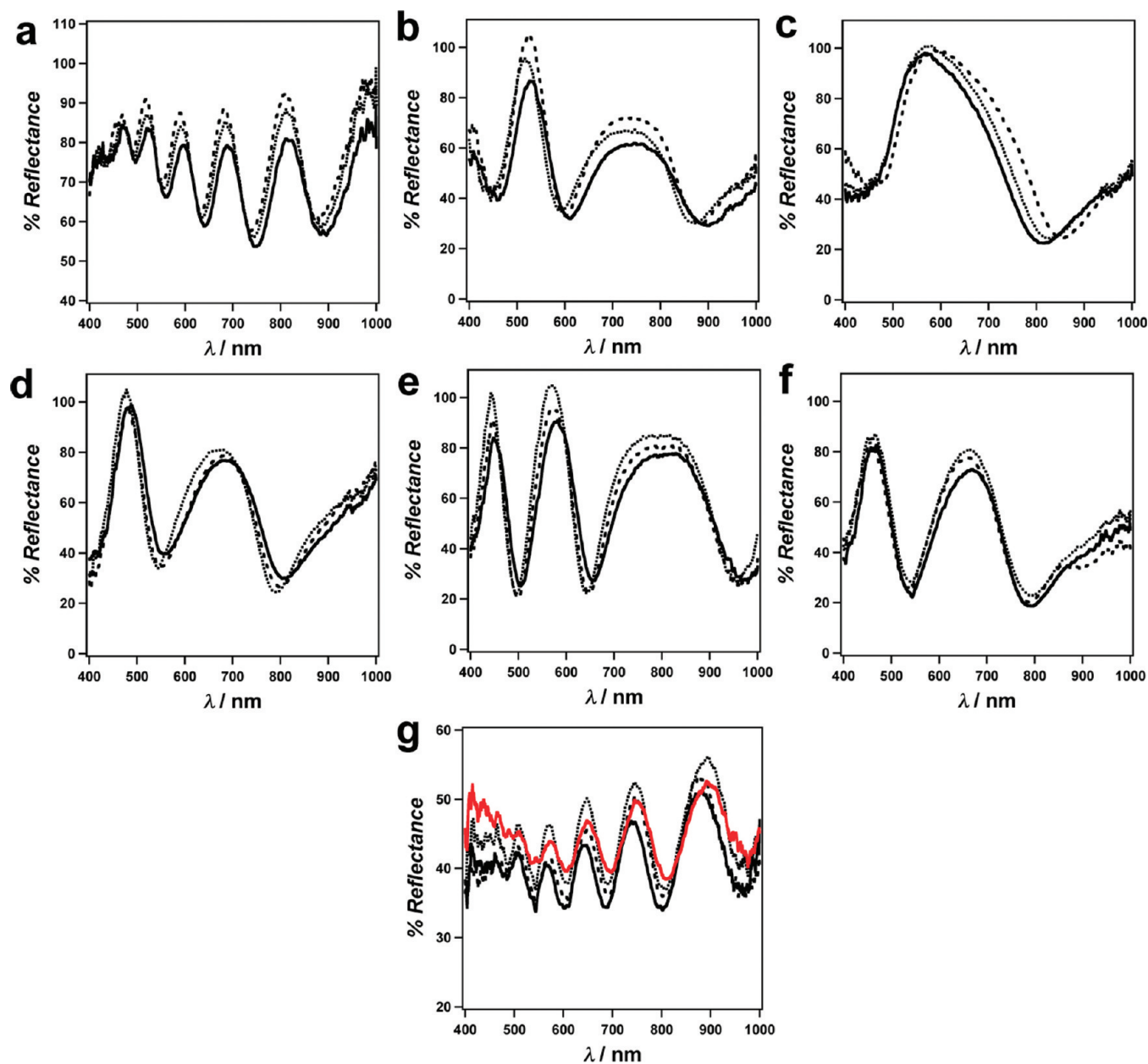
and being removed from the surface, leaving only a jammed monolayer. There is no evidence to suggest that the microgels are moving or migrating on the Au surface during soaking, indicating a very strong microgel-Au bond. We hypothesize that the Au-microgel bond is facilitated not only by weak van der Waals interactions, but also through the free electrons present on the amide N present in NIPAm. These interactions certainly lead to more robust films on Au (and presumably other metal surfaces) than SiO<sub>2</sub>. The exact nature of these interactions is under investigation and will be the subject of a future publication. Films made by the “paint-on” technique are dense and uniform, with no major defects, as can be seen in images d and e in Figure 1. The painted microgel films are also extremely robust: we have soaked painted films in water for up to 48 days with no obvious loss in microgel density or change in film morphology/structure (see the Supporting Information).

Visually, etalons made via the described “paint-on” method are more uniform than etalons fabricated using our previously described drying protocol.<sup>14</sup> This is a direct result of the increased quality of the microgel coating that serves as the dielectric layer. These painted etalons are of higher spectral quality as well. To quantify the spectral quality of the etalons generated using the two different techniques, we collected reflectance spectra over random regions of the etalons. Figure 2a shows spectra for three randomly

selected regions of an etalon generated via the “paint-on” technique. As shown, all regions display reflectance peaks at very similar wavelengths. Figure 2b shows spectra for three randomly selected regions of an etalon generated from microgels deposited via the overnight drying method. In this case, the reflectance spectra are much more variable with position on the etalon. Moreover, because some regions do not have the jammed layer of microgels required to make an etalon, no reflectance spectrum is observed in these regions; for the experiment here, only three out of four randomly chosen regions exhibited reflectance spectra.

The uniformity of the etalons made by the “paint-on” technique is further demonstrated by investigating their temperature dependent optical properties and by comparing to etalons made by our previous passive drying method. In panels c and d in Figure 2, the  $\lambda_{\text{max}}$  value of one peak in a given etalon’s spectrum is plotted as a function of temperature for three different areas on the etalon. This is done for both the etalon made by the described “paint-on” method (Figure 2a) and for the one made by our previously described drying protocol (Figure 2b). When compared to etalons made via the drying method, etalons made via the described “paint-on” method exhibit more consistent optical properties over the whole surface area, as evidenced by the similar  $\lambda_{\text{max}}$  values at all temperatures investigated. Additionally, the virtually constant phase transition temperature is independent of the etalon location being probed.

To illustrate the universality of the “paint-on” technique, we deposited microgels with varying chemical functionalities and diameters on Au coated substrates. Figure 3 shows the resulting materials. In each case the technique produces a jammed, monolithic microgel film, as seen in the DIC images. Furthermore, when a Au overlayer is deposited onto the microgel layer, a high quality etalon is produced, as seen in the photographs in Figure 3 (insets). Figure 3a–c shows etalons generated from microgels with identical chemical composition (in terms of monomer percentages), but differing microgel diameter (Table 1). DIC microscopy images reveal that the resultant



**Figure 4.** Spectra for etalons shown in Figure 3 and made from (a) pNIPAm-co-AAc-1 microgels, (b) pNIPAm-co-AAc-2 microgels, (c) pNIPAm-co-AAc-3 microgels, (d) pNIPAm-BIS, (e) pNIPAm-co-AAm microgels, (f) pNIPAm-co-VAA microgels. (g) Spectra for randomly selected regions of an etalon generated from pNIPAm-co-AAc-1 microgels on an unbent and bent flexible Au-coated transparency film. Each panel shows 3 spectra from randomly selected regions (region 1 (solid), region 2 (dotted), and region 3 (dashed line), for all graphs) of the etalons. For g, the spectrum in red is the spectrum obtained from the bent etalon. All data were collected for the etalons immersed in DI water. The spectral purity of the etalons suggests that the microgel films must be monolithic, and jammed irrespective of the underlying substrate or microgel chemical functionality.

microgel films are jammed, and apparently monolithic. Further, the photographs show the concomitant visual color when a Au overlayer is deposited. Figure 4a–c shows the reflectance spectra after a Au overlayer is deposited on the microgel layer. From the data, it is clear that each etalon is of high spectral purity, and in each case, a unique spectrum is produced with a varying number of peaks. The number of peaks likely corresponds to different Au mirror spacings, which results from differing microgel diameters. This leads to a change in the Au–Au, or mirror–mirror, spacing.

Figure 3d–f shows etalons created from microgels with different comonomer compositions. Again, it is apparent from the microscopy images that a jammed, monolithic microgel layer

is produced irrespective of microgel composition. Furthermore, when a Au overlayer is deposited, visual color is again observed. Figure 4d–f shows the spectra for the respective films collected over random regions of the etalon, again illustrating the high quality of the microgel layer, and of the resulting etalon. These data show that microgel composition and/or size is unimportant for generating quality films using the described painting protocol.

Images g and h in Figure 3 show a photograph of an etalon generated on a Au-coated flexible surface (a transparency) and Figure 3i shows the microscopy image illustrating the resultant monolithic microgel film. Evidently, the underlying substrate is not important for the technique to be effective; the only



requirement is that the substrate be coated with Au. Figure 4g shows that the microgel film deposited on the Au coated transparency produces a high quality etalon, and continues to be even when the etalon is bent (Figure 4g, red). The “bent” spectrum (red curve) shows that the red curve closely matches the spectra obtained on other regions of the unbent etalon. However, because of the nature of the measurement, we cannot be sure of how bending the etalon shifts the reflectance spectrum. This experiment was performed merely to prove that our materials behave as etalons even on a bent, flexible substrate.

Although microgel-based etalons are important for future investigations specific to our lab, the fact that jammed, monolithic microgel films can be deposited on Au-coated substrates, with extreme ease despite the size or chemical functionality of the microgels or the nature of the substrate, is of broader interest and applicability. We went on to show that the technique could be extended to coat Si surfaces with microgels, which also results in etalons when a Au overlayer is deposited on top. While this did generate an etalon, the microgel coating is not as robust when compared to those generated on Au coated substrates (see the Supporting Information).

## CONCLUSIONS

We have developed a “paint-on” technique that allows for the reproducible generation of jammed, monolithic microgel layers on Au-coated substrates. The technique appears to be universal; microgels of various chemical functionality and size can be deposited on substrates, so long as they are coated with Au. The quality of the microgel coating is evidenced by visual purity, DIC microscopy and the high spectral purity of the etalons generated after coating the microgel layer with Au. Reflectance spectra were collected over different regions of etalons generated from the “paint-on” method; they show highly consistent peak positions, which was not the case for etalons generated using our previously presented drying protocol. The “paint-on” technique is advantageous because of its ease, simplicity, and apparent universality. We are confident that this technique could easily be scaled up to coat Au-coated substrates with larger surface areas or applied to a variety of metal-coated surfaces. We also aim to extend the technique to coat Au-coated substrates with other types of polymers and materials. As we develop more optically pure and structurally complex etalons, we anticipate being able to monitor the presence of analytes and detect stimuli with the unaided eye.

## ASSOCIATED CONTENT

**S** Supporting Information. SEM images of the films made via the “paint-on” protocol; photograph and DIC microscopy image of a film painted at room temperature; DIC microscopy images of long-term soaked microgel films; DIC microscopy images of microgels attached to Au substrates after simple exposure, without drying, for various times; pictures of etalons and DIC microscopy images of films made via the drying protocol at various solution ionic strengths, pH, and solution conditions (surfactant and cosolvent concentrations); photographs of etalons fabricated on silicon and their corresponding reflectance spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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#### ■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on March, 7, 2011, with an error in Figure 4g. The corrected version was reposted on March 10, 2011.