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Two-Dimensional Photonic Crystal Surfactant Detection

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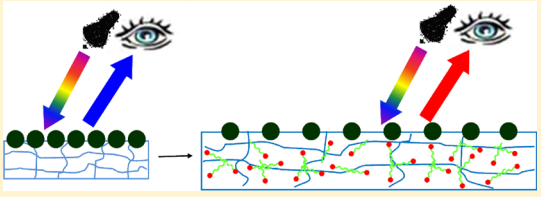
ABSTRACT: We developed a novel two-dimensional (2-D) crystalline colloidal array photonic crystal sensing material for the visual detection of amphiphilic molecules in water. A close-packed polystyrene 2-D array monolayer was embedded in a poly(*N*-isopropylacrylamide) (PNIPAAm)-based hydrogel film. These 2-D photonic crystals placed on a mirror show intense diffraction that enables them to be used for visual determination of analytes. Binding of surfactant molecules attaches ions to the sensor that swells the PNIPAAm-based hydrogel. The resulting increase in particle spacing red shifts the 2-D diffracted light. Incorporation of more hydrophobic monomers increases the sensitivity to surfactants.



Amphiphilic surfactants are organic compounds that contain both hydrophobic and hydrophilic groups. Surfactants are widely used as emulsifiers and detergents and in cosmetics, industrial cleaners, etc.[1] These applications result in release of these compounds into the environment, which impacts the environment and human health.[1,2] Therefore, there is significant interest in developing efficient detection methods for surfactants. Existing methods for determining the concentrations of surfactants in solution include titration, spectroscopy, and chromatography.[3−9] High-performance liquid chromatography (HPLC) is the preferred approach for surfactant analysis.[4−6] HPLC is somewhat expensive and requires highly trained personnel. Mass spectroscopy (MS),[7] evaporative light scattering detection (ELSD),[8] and charged aerosol detection (CAD)[9] can also be used to detect surfactants. These methods involve time-consuming sample preparation and expensive instruments. Therefore, there is a need to develop economical methods that require little sample preparation and utilize inexpensive methodologies.

In the work here, we report a new approach for the visual detection of surfactants. We utilize poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels as a substrate for surfactant molecule binding. PNIPAAm, which in water is a temperature-sensitive polymer with a lower critical solution temperature (LCST) at 32 °C, has side hydrophobic isopropyl group chains attached to hydrophilic amide groups.[10−12] The PNIPAAm-based materials have been widely investigated and utilized for drug release carriers, separations, photonic crystals, etc.[13−19]

Our two-dimensional (2-D) sensor, schematically shown in Figure 1, consists of a PNIPAAm-based hydrogel film attached to a 2-D crystalline colloidal array (CCA) monolayer of 490 nm polystyrene (PS) particles. The 2-D PS array hydrogel placed on a mirror strongly Bragg back-diffracts light of wavelengths that depend on the 2-D array spacings.[20,21] Surfactants in water solution are known to bind to PNIPAAm hydrogels through hydrophobic interactions, giving rise to ionic hydrogels.[22,23] These bound ions result in a Donnan potential that causes the hydrogel to swell. This increases the 2-D array spacing, causing a red shift in the diffracted wavelength that increases with the amount of surfactant bound.

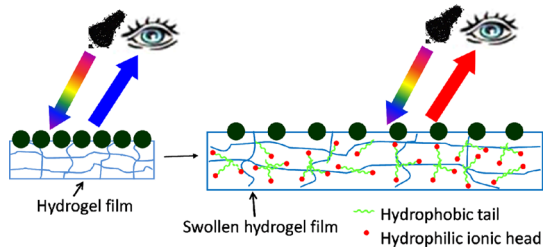


Figure 1. Schematic illustration of 2-D photonic crystal sensor formed by polymerization of a PNIPAAm hydrogel network onto a 2-D array of 490 nm PS particles on a liquid Hg surface. The PNIPAAm hydrogel swells upon binding of surfactant molecules. The 2-D particle spacing increases upon swelling of the PNIPAAm hydrogel, red shifting the diffracted wavelength.

EXPERIMENTAL SECTION

Materials. *N*-Isopropylacrylamide (NIPAAm) was purchased from Sigma-Aldrich and was purified by recrystallization in hexane. *N*,*N*′-Methylenebisacrylamide (MBAAm), hydroxyethyl acrylate (HEA), *tert*-butyl acrylate (tBA), 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959), sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS), cetyl trimethylammonium bromide (CTAB), and mercury (Hg) were purchased from Sigma-Aldrich and were used as received. Sodium C14−16 olefin sulfonate (SOS) was obtained from Stepan Company (Northfield, IL). The structures of SDS, SDBS, and SOS are shown in Figure 2. Polystyrene (PS) particles with a diameter of 490 nm were synthesized according to the literature method.[24]

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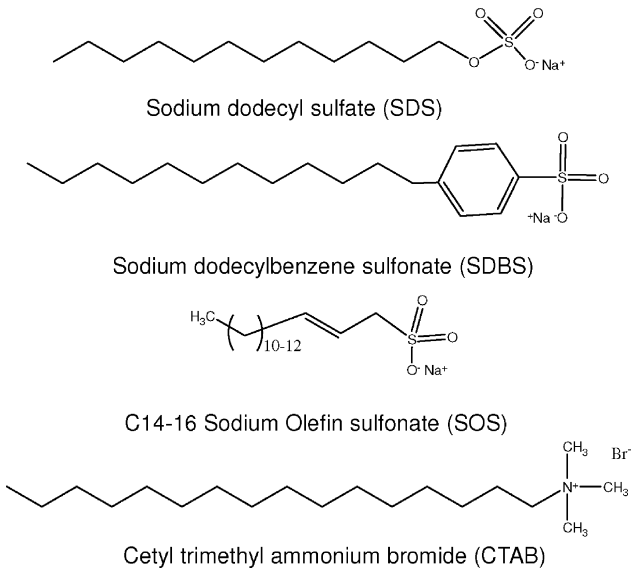

Figure 2. Chemical structures of SDS, SDBS, SOS, and CTAB.

2-D Array Sensor Preparation. The PS particle dispersion (15 wt %) and propanol were mixed at a ratio of 3:1 (in volume). A close-packed 2-D PS array was fabricated on a Hg surface through the self-assembly of colloidal PS particles during spreading of the particle dispersion.[20,25] A 1 mL reaction mixture consisting of NIPAAm (10 wt %) and MBAAm (0.2 wt %) in Nanopure water was mixed with 20 μL of Irgacure 2959 (in DMSO, 33% (w:v)). This polymerization solution was layered onto the 2-D array monolayer on the Hg surface. A glass slide (60 mm × 24 mm × 0.12 mm) was placed onto the reaction solution. The polymerization was initiated by UV light (UVGL-55 hand-held UV Lamp, UVP, Upland, CA). The resulting 2-D array PNIPAAm-based hydrogel film was lifted from the Hg surface, peeled from the glass slide, and rinsed with large amounts of water. The hydrogel film was equilibrated in water for at least 24 h, during which the water was frequently replaced. The thickness of the swollen hydrogel sensor is between 500 and 600 μm.

The PNIPAAm gel was made more hydrophobic by incorporating HEA or tBA monomer. Different amounts of HEA and tBA (5 vol% in DMSO) were added to the NIPAAm reaction solutions, and the reaction mixtures were cooled in an ice bath before polymerization. Ice was also packed around the Petri dish containing the 2-D array on Hg to prevent phase separation during polymerization. This is critical because the hydrophobic monomers decrease the hydrogel LCST. Polymerization at higher temperatures results in phase-separated, white, and opaque hydrogels. The chilled reaction solution was layered onto the chilled 2-D array monolayer and polymerized.

Diffraction Measurements. Diffraction of the 2-D polymerized CCA was monitored by using an Ocean Optics USB2000-UV−Vis spectrometer, a LS-1 tungsten halogen light source, and an R-series fiber optic reflection probe. The diffraction measurements were carried out in a Littrow configuration with a 28° measurement angle between the probe and the normal to the 2-D array. Surfactants were dissolved in Nanopure water (18.2 MΩ). The surfactant concentrations ranged from 0 to 20 mM. The hydrogel sensors were immersed in 20 mL surfactant solutions. After equilibration at room temperature, the 2-D array PNIPAAm-based hydrogel sensors in surfactant solutions were taken out and placed on front surface silver mirrors (Thorlabs, Sterling, VA) for the diffraction measurements. The measurement was carried out at room temperature.

RESULTS AND DISCUSSION

In the Littrow configuration, the 2-D array Bragg diffraction condition is $m\lambda = 3^{1/2} \times d \sin\theta$, where m is the diffraction order, λ is the wavelength of the diffracted light, d is the nearest neighboring particle spacing, and θ is the angle between the incident light and the normal to the 2-D array. For a fixed incidence angle θ, the diffracted wavelength, λ, is proportional to the 2-D particle spacing, d.

Surfactant binding to the PNIPAAm hydrogel results in attachment of charged groups to the hydrogel. This bound hydrogel charge and its counterions give rise to a Donnan potential that increases the hydrogel osmotic pressure, resulting in a hydrogel volume increase and an increase in the spacing of the 2-D particles, d, that red shifts the diffraction.

Anionic surfactants account for 50% of the surfactant used in Europe and 60% in US.[1,26] We examined the response of our sensors to three anionic surfactants, SDS, SDBS, SOS, and cationic surfactant, CTAB. When the sensing hydrogel is placed in the surfactant solution, the surfactant molecules diffuse into the hydrogel network. Strong binding takes place through the hydrophobic interactions between the PNIPAAm and the surfactant hydrophobic tails.[27,28] As a result, the volume of the hydrogel sensor increases with surfactant binding, and the diffraction red shifts.

Figure 3a shows the dependence of the 2-D array PNIPAAm-based hydrogel sensor diffraction spectra on the SDS concentration in aqueous solutions. In pure water the 2-D array PNIPAAm-based hydrogel sensor diffracts at 470 nm. The diffracted wavelength red shifts to 500 nm in 1 mM SDS. Increasing the concentration to 5 mM further shifts the diffraction to 622 nm. Figure 3b shows the dependence of the 2-D diffraction wavelength and color on the SDS concentration.

The critical aggregation concentration (CAC) of a surfactant to a polymer is the concentration where the surfactant forms polymer-bound micelles. The CAC is lower than the solution critical micelle concentration (CMC). The SDS CAC is reported to be ∼0.79 mM for PNIPAAm hydrogels.[28] At low SDS concentrations (≤0.5 mM) there is little binding of SDS to PNIPAAm, the hydrogel volume does not change, and the diffraction wavelength of the 2-D array remains similar to that in pure water (Figure 3). However, at SDS concentrations above the CAC, surfactant binding to the hydrogel attaches charged surfactants that induce a Donnan potential that swells the hydrogel.[29] For example, the diffraction wavelength shifts to 500 nm for 1 mM SDS solution. The inset in Figure 3b illustrates the visually evident color changes of the surfactant sensor at the different SDS concentrations.

Figure 4 also shows the concentration dependence of the diffraction wavelength shift of the 2-D sensor for SDS, SDBS, and SOS surfactants of different hydrocarbon lengths. With increasing surfactant concentrations, the amount of bound surfactant to the hydrogel increases, which causes the hydrogel to swell and the diffraction to shift to longer wavelengths. However, at high concentrations (>5 mM), the surfactant molecules form free micelles that increase the solution ionic strength which decreases the hydrogel swelling[29] and the 2-D particle spacing, causing the diffraction to blue shift.

Figure 4 shows that the 2-D hydrogel sensor is most sensitive to SDBS. Moreover, for surfactant concentrations below 5 mM,

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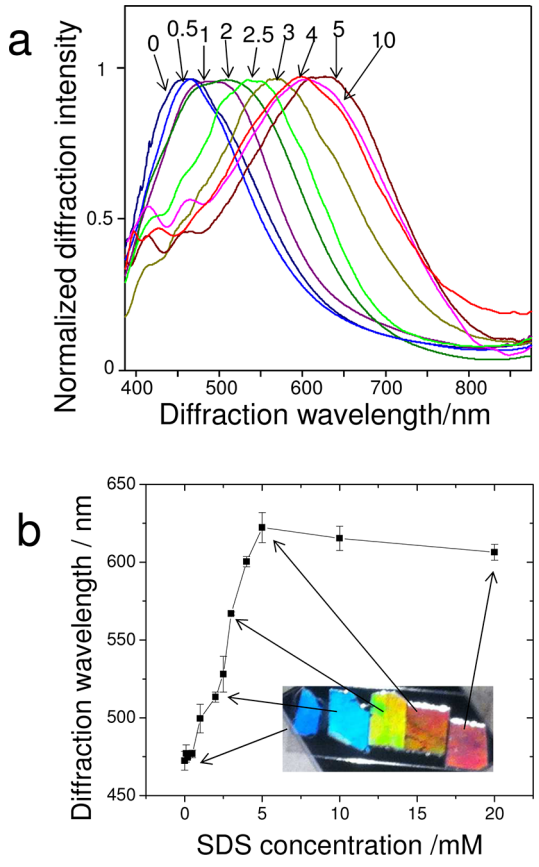

Figure 3. (a) Normalized and smoothed diffraction spectra of 2-D PNIPAAm sensors at different concentrations of aqueous SDS solutions. The spectra were measured with 40 ms accumulations. The measurement angle between the probe and the normal to the 2-D array is 28°. (b) Diffraction wavelength versus SDS concentration. The inset shows photographs taken close to the Littrow configuration at an angle of 28° between the source and camera to the 2-D array normal.

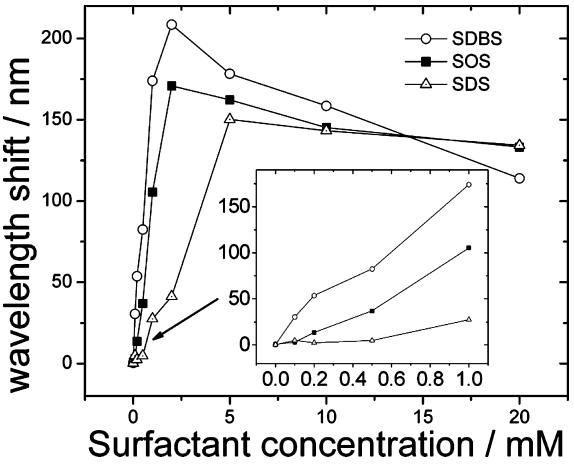

Figure 4. Dependence of the diffraction red shift on the concentrations of surfactants SDS, SDBS, and SOS. The inset expands the low concentration regime. The spectra were measured with 40 ms accumulations.

the diffraction red shifts most for surfactants of largest hydrocarbon chain length (SDBS (18C) > SOS (14−16C) > SDS (12C)). For example, at 1 mM surfactant concentrations, the SDBS, SOS, and SDS wavelength red shifts are 174, 105, and 30 nm, respectively. This is because the surfactant hydrophobic binding affinity increases with increasing surfactant chain length. Our results are consistent with hydroxyethyl cellulose hydrogel swelling observed in surfactant solutions, where longer surfactant alkyl lengths show increased swelling.[29,30]

Our 2-D hydrogel sensors also sense cationic surfactants. Figure 5a shows the diffraction spectra of 2-D PNIPAAm

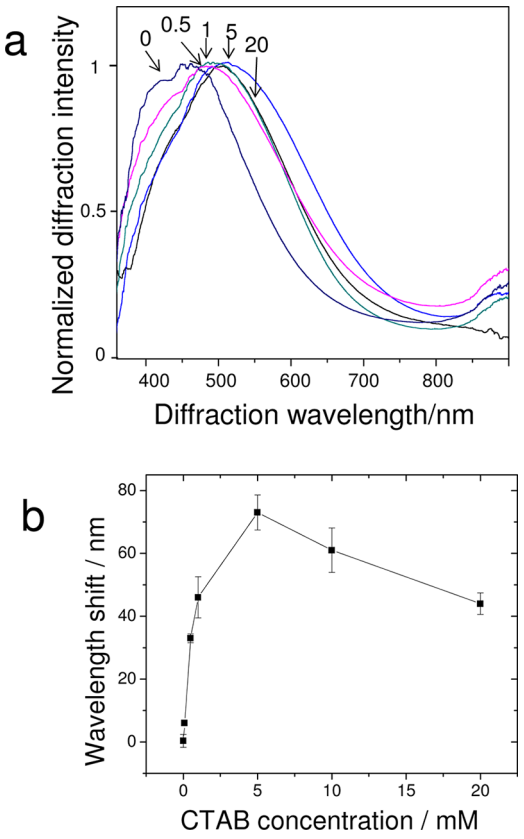

Figure 5. (a) Normalized and smoothed diffraction spectra of 2-D PNIPAAm sensors at different concentrations of aqueous CTAB solutions. The measurement angle between the probe and the normal to the 2-D array is 28°. (b) The diffraction red shift versus the concentrations of CTAB.

sensors at different CTAB concentrations, while Figure 5b shows the concentration dependence of the diffraction shift of the 2-D sensor for cationic CTAB. The diffraction wavelength shifts about 70 nm when increasing the CTAB concentration from 0 to 5 mM because CTAB binds to the PNIPAAm hydrogel.[31] At higher concentrations (10 and 20 mM), the diffraction blue shifts because the surfactant binding reaches saturation. Note that the peak shift of the 2-D sensors in the cationic CTAB solution is less than that in anionic surfactants. This is possibly due to the smaller hydrophilicity of the CTAB trimethylammonium ionic head groups. Our results agree with the previously reported swelling of PNIPAAm hydrogel in CTAB.[32]

Copolymerization of hydrophobic monomers into the NIPAAm hydrogels increases the sensor sensitivity to surfactant. We copolymerized hydrophobic HEA and tBA into the PNIPAAm hydrogels to increase their hydrophobicity. Figure 6a shows the dependence of the diffraction wavelength on the HEA and tBA content. The diffraction of the 2-D hydrogels in water blue shifts with increasing hydrophobic

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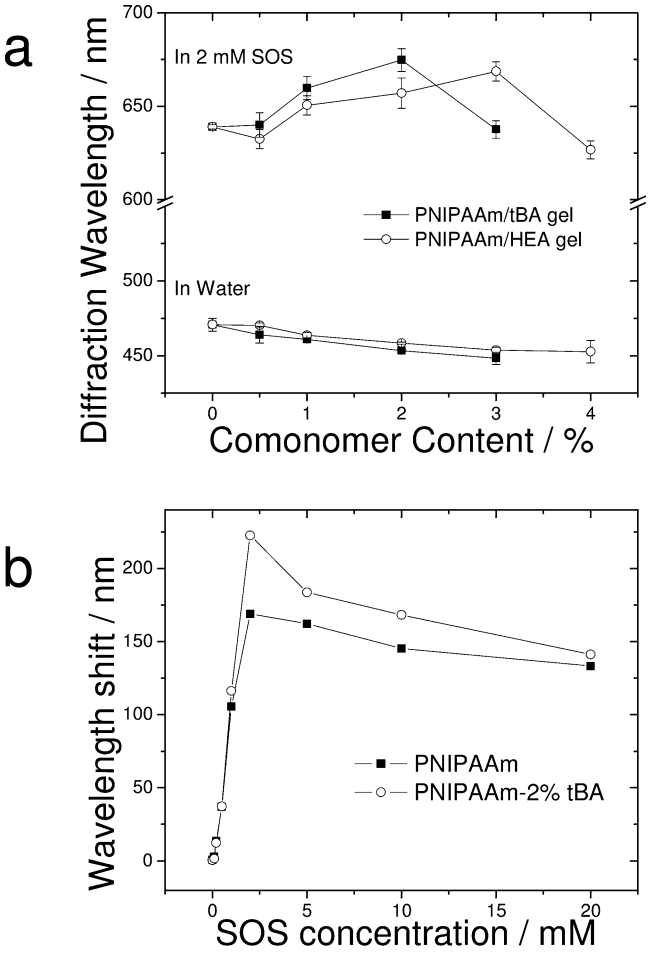

Figure 6. (a) The impact of HEA and tBA content on the 2-D PNIPAAm-based hydrogel diffracted wavelength in 2 mM SOS solution. (b) SOS concentration dependence of the diffraction wavelength shift of PNIPAAm and PNIPAAm/tBA (2%)-based hydrogel sensors.

monomer content because the hydrogel free energy of mixing with water decreases.

In 2 mM SOS, the diffraction red shifts and then blue shifts as the content of hydrophobic monomers increases. For example, the 2-D array PNIPAAm/HEA hydrogel sensor diffracts at 632, 650, 657, and 669 nm at 0.5%, 1%, 2%, and 3% HEA content, respectively. However, an increase in the HEA content to 4% causes a diffraction blue shift to 627 nm (Figure 6a) because the increased amount of comonomer, HEA, increases the hydrophobicity of the hydrogel. Binding of SOS does not overcome this large increase in hydrophobicity. Therefore, at 4% HEA and 3% tBA content, the hydrogel swelling in 2 mM SOS is decreased and the diffraction is blue-shifted.

The 2-D PNIPAAm/tBA hydrogel sensor shows a similar behavior. These hydrophobically modified 2-D PNIPAAm sensors likely bind more surfactant, causing higher swelling and red shifts.[23] For the tBA-modified PNIPAAm-based hydrogel sensor, the diffraction maximum occurs at lower copolymer content than for HEA because tBA is more hydrophobic than HEA.

Figure 6b shows the concentration dependence of the diffraction wavelength shift of pure PNIPAAm and PNIPAA 2-D sensors containing 2% tBA in SOS. With increasing SOS concentrations, the hydrogels swell, which red shifts the diffraction to longer wavelengths. At high concentrations, the diffraction blue shifts due to the formation of free micelles that decrease the swelling of the hydrogel. The diffraction shift of PNIPAA/tBA hydrogel-based sensor is larger than that of the PNIPAAm-based hydrogel sensors because copolymerization of tBA increases the binding of SOS to PNIPAA/tBA hydrogels. Therefore, we can conclude that the sensor sensitivity which is defined as the diffraction shift divided by the surfactant concentration is increased by the incorporation of hydrophobic monomers.

CONCLUSIONS

We developed a photonic crystal sensing material that can be used to visually determine the concentrations of anionic and cationic surfactants such as SDS, SOS, SDBS, and CTAB in water. The sensor material consists of 2-D PS particle arrays on a PNIPAAm-based hydrogel. Binding of ionic surfactant molecules to PNIPAAm polymer chains attaches ions that induce a Donnan potential that swells the hydrogel and increases the 2-D particle spacing, red shifting the diffracted light. Incorporating hydrophobic monomers into the hydrogel increases the sensor sensitivity.

Our 2-D photonic crystal sensing materials can detect ~0.1 mM concentrations of surfactants. The detected concentration range covers the surfactant concentrations present in municipal sewer discharges (20–70 mg/L)[33,34] and in industrial wastewater (300 mg/L).[35]

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Notes

The authors declare no competing financial interest.

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