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Centrifugation-Induced Water-Tunable Photonic Colloidal Crystals with Narrow Diffraction Bandwidth and Highly Sensitive Detection of SCN⁻

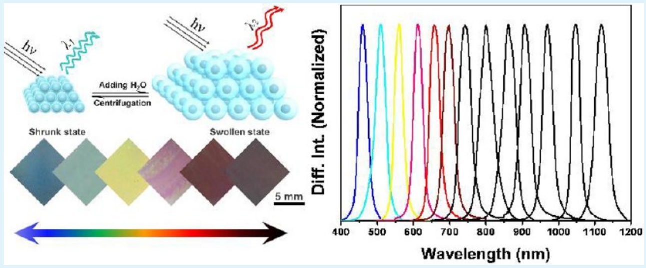
Cheng Ma,[†] Yingnan Jiang,[§] Xudong Yang,[†] Chuanxi Wang,[†] Hui Li,[†] Fengxia Dong,[†] Bai Yang,[†] Kui Yu,[*,‡] and Quan Lin[*,†]

[†]State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, 130012, P. R. China

[§]Lab of Polymer Composites Engineering, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

[‡]Emerging Technologies, National Research Council of Canada, Ottawa, Ontario, K1A 0R6, Canada

Supporting Information



ABSTRACT: Novel opal hydrogels with water-tunable photonic bandgap (PBG) exhibiting responses to external stimuli were self-assembled from polystyrene-*co*-poly(*N*,*N*-dimethylacrylamide) (PS-*co*-PDMAA) microspheres. The polymeric microspheres with narrow size distribution were successfully prepared in water, consisting of two regions. The inner region is rich in PS which is hard and hydrophobic; the outer region is rich in PDMAA which is soft and hydrophilic. The self-assembly of the PS-*co*-PDMAA hydrogel microspheres is ready induced by centrifugation and resulted in highly ordered three-dimensional (3D) photonic colloidal crystals (PCCs). With an increase of the amount of water, the PBG of the opal hydrogels shifted from the visible to near-infrared region of the electromagnetic spectrum. The maximum shift of diffraction peak positions could be larger than 500 nm with narrow full width at half maximum (FWHM) in the range of 20 to 40 nm only. The change in color was visible to the naked eye. The remarkable sensitivity to water of the lattice spacing of the opal hydrogels was repeatable after centrifugation. These observations are attributed to a reproducible degree of hydration of the hydrophilic outer region of the polymeric microspheres. Furthermore, the diffraction of the opal hydrogels was particularly sensitive to the presence of thiocyanate (SCN⁻) ions. The interaction between SCN⁻ ions and DMAA repeat units is argued to block hydrogen bonds between DMAA and water molecules. Our PS-*co*-PDMAA opal hydrogels could be a practical system for diffraction-based detections.

KEYWORDS: *photonic colloidal crystals (PCCs), stimuli-responsive opal hydrogels, self-assembly, photonic bandgap (PBG), SCN⁻ ion detection*

■ INTRODUCTION

Colloidal photonic crystals have been investigated significantly over the past decade, together with the synthesis of polymeric colloidal microspheres and their self-assembly leading to 3-dimentional ordered arrays.[1−47] The variation of the periodic structures can tune light propagation, which holds technological implications in various areas,[1−30] such as telecommunication, switch, optical fibers, display devices, biological detection, and chemical sensors. Much progress has been made in the fabrication of polymeric colloidal crystal arrays that are responsive to external stimuli, which result in the modification of the lattice spacing of the opal structures. Accordingly, the wavelength of diffraction of these photonic colloidal crystals (PCCs) shifts due to the change of photonic band gap (PBG). For diffraction-based applications, it is critical to engineer PCCs to exhibit bright and structure-based color.

Up to now, there are three types of responsive PCCs documented mainly.[31−47] The first two are non-close-packed crystal films and inverse opal films, both of which are formed via crosslinking of various hydrogels. Their PBG has been reported to respond to external stimuli, including mechanical force, metal ions, pH, glucose, and electrical fields.[31−42] Unfortunately, the swelling degree of these films has been seriously limited due to their rigid structures resulted from crosslinking. Accordingly, it remains challenging to engineer crosslinked hydrogel films to exhibit substantial variation of their PBG. The third type of responsive PCCs is close-packed microgel opals commonly constructed from the self-assembly of

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poly(*N*-isopropylacrylamide) (PNIPAM) microspheres.[43−47] Most PNIPAM-based PCCs experience a problematic volume change near the PNIPAM lower critical solution temperature (LCST). Consequently, their crystal lattices are vulnerable to collapse and become disordered. During responses to external stimuli, it is not easy for the PNIPAM-based PCCs to maintain their narrow bandwidth diffraction and thus color purity. Since 2006, a new type of polymeric hydrogels of poly *N*,*N*-dimethylacrylamide (PDMAA) has attracted attention in our group and other research groups for their water-swollen and stimuli-responsive properties.[48−52]

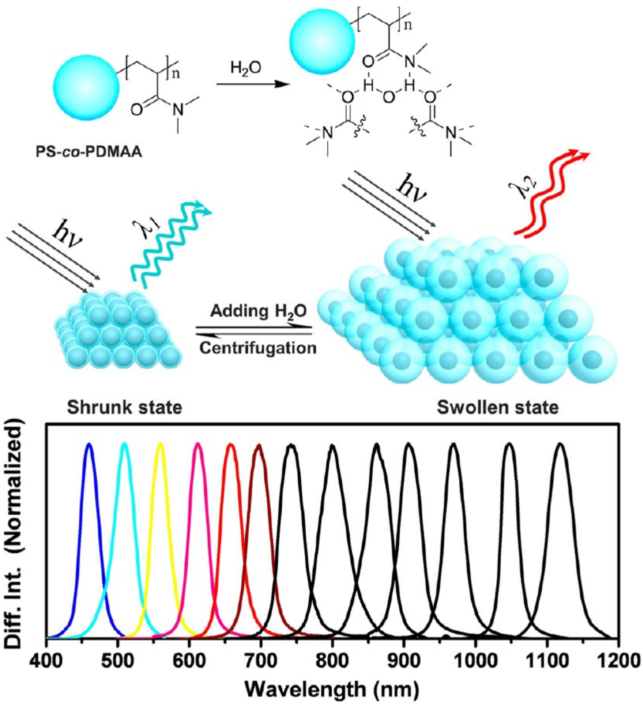
Herein, we report our successful preparation of a novel smart hydrogel composed of polystyrene-*co*-poly(*N*,*N*-dimethylacrylamide) (PS-*co*-PDMAA) microspheres, which have inner regions rich in hard and hydrophobic PS and outer regions of soft and hydrophilic PDMAA. With narrow size distribution, the synthesized PS-*co*-PDMAA hydrogel microspheres self-assembled readily, during centrifugation, leading to the formation of opal hydrogels. Numerous acrylamide groups on the surface of the microspheres resulted in high surface hydrophilicity. The opal hydrogels responded rapidly and sensitively to the amount of water presented, producing diffraction with high color purity. The volume of the opal hydrogels increased continuously with an increase of the amount of water and decreased with a decrease of the amount of water. Such a reversible swelling and shrinking behavior induced by the change of the amount of water was accompanied by the rapid PBG alteration of the opal hydrogels and consequent red and blue shift of their diffraction, respectively. The diffraction could shift its peak position larger than 500 nm and retain still very much narrow full width at half maximum (FWHM) in the range of 20 to 40 nm, as shown in Scheme 1. The opal hydrogels are sensitive to the presence of thiocyanate (SCN^-) ions selectively and quantitatively; the interaction between SCN^- ions and the DMAA repeat units suppressed the interaction between the DMAA repeat units and water molecules. These novel and smart opal hydrogels with sensitive, reversible, and repeatable responses to external stimuli should be applicable to the construction of diffraction-based sensors.

■ EXPERIMENT AND CHARACTERIZATION

Materials. *N*,*N*-Dimethylacrylamide (DMAA, Aldrich) and sodium dodecyl sulfate (SDS, Aldrich) were used without further purification. Styrene (St, Aldrich) was purified by vacuum distillation to remove its stabilizer. Potassium persulfate (KPS) as an anionic initiator was purified by crystallization from water. Water was purified by a Millipore Milli-Q system.

Preparation of PS-*co*-PDMAA Microspheres and PCCs. The polystyrene-*co*-poly(*N*,*N*-dimethylacrylamide) (PS-*co*-PDMAA) microspheres were prepared by an emulsion polymerization.[53,54] A mixture of St, DMAA, and SDS was added into 130 mL of deionized water into a 250 mL three-necked round-bottom flask, which was equipped with a condenser, a nitrogen inlet, and a stirrer. The mixture was stirred under nitrogen at room temperature for 30 min to remove oxygen in the system. Polymerization was initiated at 70 °C by the addition of 20 mL of an aqueous solution containing $K_2S_2O_8$ (~7.5 mg/mL). The reaction was allowed to proceed for 8 h at 70 °C. The PS-*co*-PDMAA hydrogel microspheres obtained had a narrow size distribution and were further purified by dialysis and repetitive centrifugation. Finally, they were dispersed in water. Three samples of the PS-*co*-PDMAA hydrogel microspheres are presented and denoted as P1, P2, and P3. See Table S1, Supporting Information, for experimental details and Table S2, Supporting Information, for their compositional information obtained from elemental analysis. Centrifugation resulted in PCCs of the PS-*co*-PDMAA microspheres. The as-prepared opal hydrogels exhibited bright composition dependent color which could be observed by the naked eye.

Scheme 1. Schematic Drawing of the Formation of Hydrogen Bonds between Water and the Amide Side Groups of the DMAA Repeat Units of the Surface PDMAA of PS-*co*-PDMAA Microspheres[a]



[a] The water-induced red shift of the diffraction of the centrifugation-induced PCCs is related to the swelling behavior of the PS-*co*-PDMAA PCCs, which exhibit narrow diffraction bandwidth.

Water-Tunable PCCs with Narrow Diffraction Bandwidth. The PBG of the PS-*co*-PDMAA colloidal crystals displayed red shifts upon the addition of water. After centrifugation, for example, 0.13500 g of P2 hydrogel was placed in a depression in a quartz plate. Deionized water (0.05 mL) was added into the bath. After a 1 minute (min) ultrasound, a diffraction spectrum was collected. The procedure of 0.05 mL of water addition, 1 min ultrasound, and spectrum collection was repeated until the disappearance of the opal structure.

Detection of SCN^- and Other Ions. The PBG of the opal hydrogels is sensitive to the presence of SCN^- ions in water. For example, after centrifugation, 0.30000 g of P3 hydrogel was treated the same as described above for P2 but with 1.85 mL of water or a solution added to a water content of ~85% of the system by weight. In total, nine SCN^- solutions were investigated with the concentrations of $K \times 10^{-5}$ mol/L, where K = 0, 1, 5, 10, 50, 100, 300, 600, and 800, demonstrating that a quantitative detection of SCN^- (of 0, 8.6, 43, 86, 430, 860, 2600, 5200, and 6900 nmol/g, respectively) could be achieved. For comparison, 1.85 mL of eight other 10^{-3} mol/L solutions of Na_2SO_3, NaF, Na_2NO_3, Na_2CO_3, NaCl, Na_2CrO_4, $NaNO_2PhSO_3$, and $NaHCO_3$ was explored.

Characterization. UV-vis-NIR reflected spectra were acquired using a Shimadzu 3600 UV-vis-NIR spectrophotometer. Scanning electron microscopy (SEM) was performed with a JEOL FESEM 6700F electron microscope with primary electron energy of 3 kV. AFM images were recorded in a tapping mode under ambient conditions with a Multimode Nanoscope III scanning probe microscope from Digital Instruments. Transmission electron microscopy (TEM) was conducted using a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD cinema. IR spectra were taken on a Nicolet AVATAR 360 FT-IR

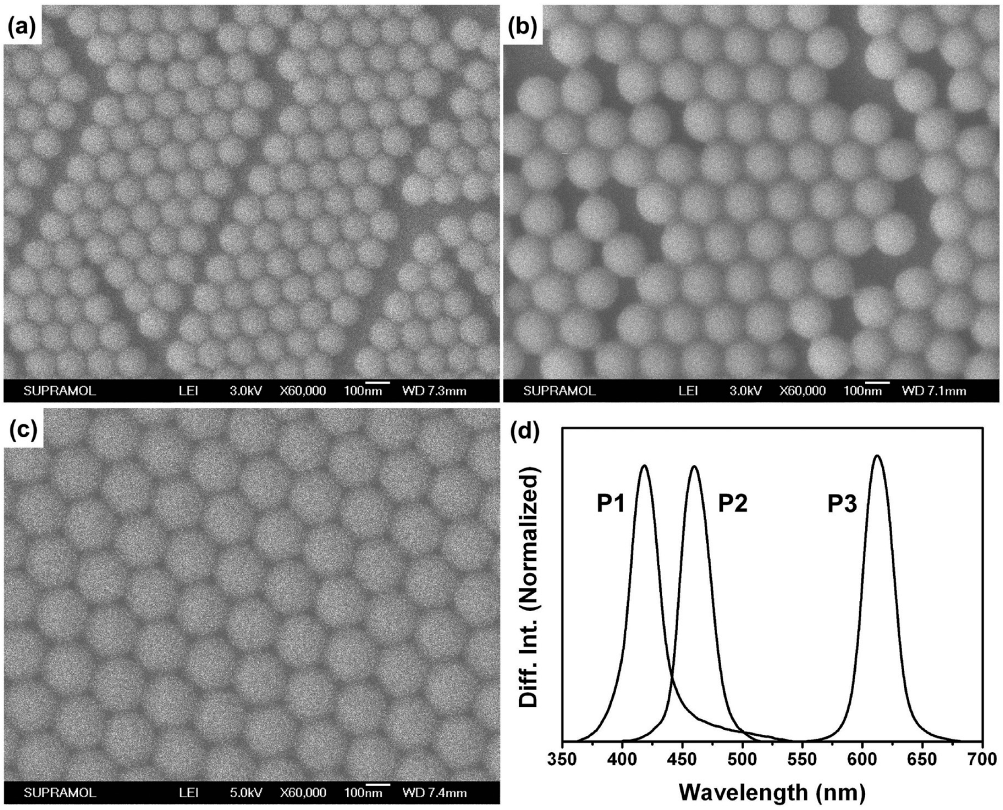


Figure 1. SEM images of P1 (a), P2 (b), and P3 (c). Diffraction spectra (d) of the three PCCs induced by centrifugation.

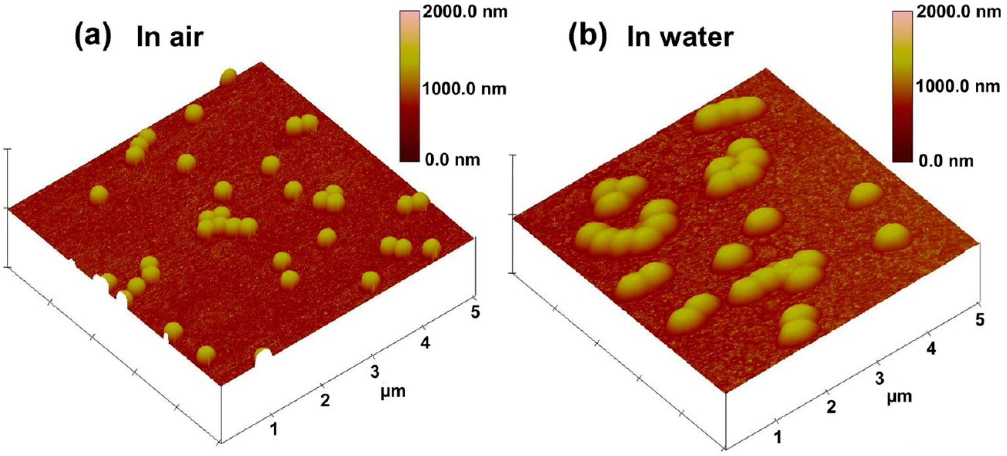


Figure 2. AFM images of P3 obtained in air (a) and in water (b), demonstrating ~371 and ~706 nm in diameter, respectively, as also shown in Figure S2, Supporting Information. It is clear that the P3 microspheres can swell to a large degree.

spectrophotometer, and ^{1}H NMR spectra were recorded on a Bruker Ultra Shield 500 MHz. Dynamic light scattering (DLS) measurements were performed using a Zetasizer NanoZS (Malvern Instruments). Elemental analysis was taken on a VarioMICRO.

RESULTS AND DISCUSSION

Structure and Self-Assembly of PS-*co*-PDMAA Microspheres. Emulsion polymerization resulted in sub-micrometer sized PS-*co*-PDMAA microspheres.[53,54] These microspheres exhibited narrow size distribution with hard and hydrophobic PS rich in their inner regions and soft and hydrophilic PDMAA in their outer regions. Figure 1 shows three SEM images of the P1, P2, and P3 samples of the PS-*co*-PDMAA microspheres; another three SEM images with smaller magnification and three TEM images are presented in Figure S1-1, Supporting Information. The estimated SEM sizes are ~138, ~181, and ~215 nm, respectively. The estimated TEM sizes are ~133, ~179, and ~204 nm, respectively. The TEM images show a common phenomenon that the inner regions seem to be relatively dense, as compared to the outer regions.[55,56] Figure S1-2, Supporting Information, presents TEM images of the microspheres sampled at different growth periods, illustrating the growth in size of the PS-*co*-PDMAA microspheres. Figure S1-3, Supporting Information, shows dynamic light scattering measurements of Samples P1, P2, and P3, demonstrating narrow size distribution and an increase in size from P1, P2, to P3. These PS-*co*-PDMAA hydrogel microspheres self-assembled into an opal structure during centrifugation; from P1 to P2 to P3, their PBG red shifts, as demonstrated by Figure 1d showing narrow FWHM of their diffraction spectra.

The FTIR spectra of P1 PS-*co*-PDMAA microspheres, PS microspheres, and DMAA monomers are presented in Figure S1-4, Supporting Information. For PS microspheres, the characteristic absorption peaks at 3100−3000, 757, and 700 cm^{-1} represent the vibrations of C−H bonds at different positions. For DMAA monomers, the characteristic absorption peaks at 1139 and 1721 cm^{-1} are attributed to C−N and C=O bonds, respectively. These characteristic absorption peaks can be found in the FTIR spectrum of the PS-*co*-PDMAA microspheres. The FTIR spectra support the formation of the PS-*co*-PDMAA microspheres by the copolymerization of the monomers of St and DMAA. Figure S1-5, Supporting Information, shows the ^{1}H NMR spectra of the PS-*co*-PDMAA microspheres in D_2O and $CDCl_3$. The P1 microspheres dispersed in D_2O displayed no signals of phenyl protons but a lot in $CDCl_3$. The ^{1}H NMR results suggest that PS-*co*-PDMAA existed as microspheres in D_2O while linear copolymers were in $CDCl_3$. Moreover, the PS-*co*-PDMAA microspheres in D_2O have two regions, one rich in PS which is hydrophobic, the other rich in PDMAA which is hydrophilic.

Water-Tunable PBG of PS-*co*-PDMAA PCCs with Narrow FWHM. Figures 2 and S2, Supporting Information, show AFM images obtained in air and in water of the P3 microspheres. The microspheres were spin-coated together with polyvinyl alcohol (PVA) for the immobilization on AFM substrates. The presence of PVA suppressed the self-assembly of the microspheres; without the use of PVA, the microspheres floated in water and contaminated our AFM tip. The AFM diameter in air is ∼371 nm and in water is ∼706 nm. Clearly, the AFM diameter of ∼371 nm is larger than the TEM diameter of ∼204 nm. Such difference in size could be attributed to the characterization environment: TEM in vacuum and AFM in air with a thin film of PVA on its substrate. For the AFM measurement, such an increase of ∼335 nm in the diameter in water supports that our hydrogel microspheres are hydrophilic with surface rich in PDMAA. As shown in Scheme 1, hydrogen bonds are formed between the microspheres and water via the acrylamide groups of the DMAA repeat units,[51] leading to substantial sensitivity in volume to the amount of water. A maximum increase of the AFM volume of the P3 microspheres from air to water could reach ∼700%.

It has been well acknowledged that microsphere sizes play a significant role on the PBG of their resulting PCCs.[8,9,28,30] Accordingly, we tested, by diffraction, water tunability of centrifugation-induced PCCs of the PS-*co*-PDMAA microspheres. The addition of water resulted in an enlargement of the size of the microspheres; consequently, the lattice spacing of the PCCs increased, as shown by Scheme 1. Figure 3a shows six digital photos of the P2 hydrogels; with six amounts of water added from 27% to 85% by weight, the P2 hydrogels exhibited blue to dark-red. Figure 3b presents their corresponding diffraction spectra, peaking at 460, 510, 560, 610, 660, and 740 nm with narrow FWHM of 28, 32, 28, 23, 21, and 37 nm, respectively. The narrow FWHM suggests the preservation of the ordered structure during the addition of water.[57]

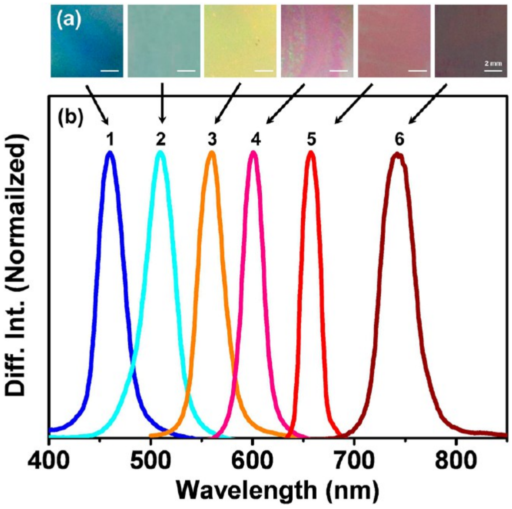


Figure 3. Digital photos (a) and corresponding diffraction spectra (b, normalized) of the P2 opal hydrogels with the five amounts of water added, as indicated. The PCCs with the six amounts of water added from 27% to 85% (as indicated by weight) seem to exhibit the color of blue, green, yellow, pink, red, and dark-red, respectively.

The PBG of P3 is larger than that of P2, as shown by Figure 1d. Thus, the water tunability was also tested with the P3 hydrogels. Figure 4a shows 10 diffraction spectra collected from the P3 hydrogels with water added of 18% (1), 60% (2), 66% (3), 74% (4), 78% (5), 80% (6), 82% (7), 86% (8), 90% (9), and 93% (10) by weight. During the red shift of the diffraction spectra from 610 nm (1) to 1120 nm (10), the FWHM stayed narrow with the estimation of 28, 30, 33, 35, 41, 38, 34, 31, 26, and 40 nm, respectively. Figure 4b shows the diffraction peaks obtained at various water amounts investigated.

It is intriguing to understand the peak shift. The diffraction peak position ($\lambda_{\max}$) of PCCs was estimated by eq 1,[9,28,38,58−60]

$$k\cdot\lambda_{\max} = \left(\frac{8}{3}\right)^{1/2} d\cdot n_{\mathrm{eff}}\cdot\sin\theta \tag{1}$$

where k is the order of Bragg diffraction and θ is the glancing angle between the incident light and diffraction crystal planes. In our study, $k = 1$ and θ is fixed at 90°. Thus, there are two factors affecting $\lambda_{\max}$, d the diameter of microspheres and n_{eff} the average refractive index of PCCs. When water was added, the red shift of $\lambda_{\max}$ was claimed to be a pure consequence of the increase of d, with the change of n_{eff} alone leading to 1−2 nm blue shift.[38,59,60]

Importantly, the diffraction red shift of our PCCs was repeatable after centrifugation and the addition of water. Figure 4c summarizes the peak positions of the P3 hydrogels during five cycles of centrifugation and water addition. Each centrifugation resulted in 0.45000 ± 0.02000 g of P3 followed by six steps of water addition from 18% to 93% by weight. Figure S3, Supporting Information, shows the diffraction spectra acquired during each of the five cycles. Clearly, the diffraction peak position is determined by the amount of water added. The re-use capability data support our understanding of Scheme 1 and eq 1: the diffraction peak position depends on the microsphere size, which is related to the amount of water added.

Selective and Quantitative Detection of SCN^-. Thiocyanate (SCN^-) has been administered as drug in the treatment of thyroid conditions[61] and has been reported to achieve an optimal antibacterial effect in a lactoperoxidase system of milk.[62] Therefore, the detection of SCN^- in food, waste water, and biological samples is of considerable importance.[61,63,64] Figure 5a shows the red shift of the

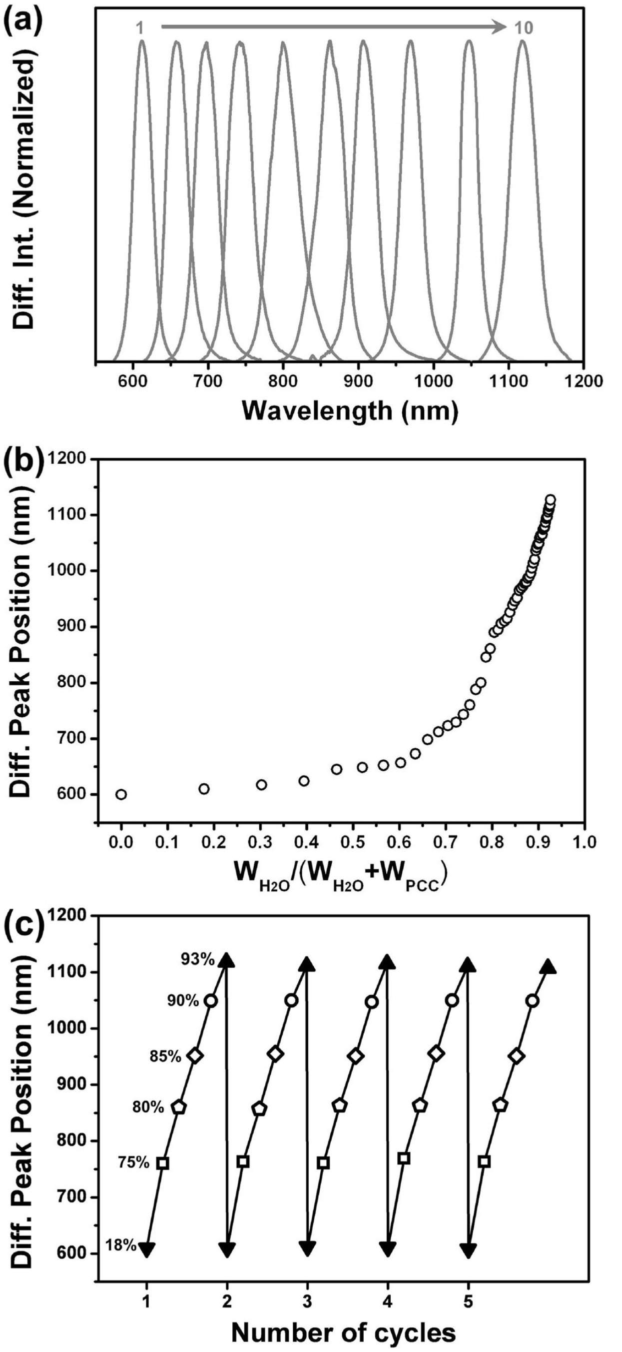


Figure 4. (a) Diffraction spectra of the P3 PCCs upon the addition of water of 18% (1), 60% (2), 66% (3), 74% (4), 78% (5), 80% (6), 82% (7), 86% (8), 90% (9), and 93% (10) by weight. (b) Summary of the diffraction peak positions of the P3 PCCs at different water amounts studied. (c) The red shift of the diffraction peak position of the P3 PCCs was tested to be repeatable with five cycles of centrifugation and water addition by weight of 18% (▼), 75% (□), 80% (⬠), 85% (◇), 90% (○), and 93% (▲) in each cycle.

diffraction peak position of the P3 PCCs with the addition of 85% of water by weight. Nine water solutions were investigated with the same concentration of 1 × 10^{-3} mol/L. Among the nine sodium salts of SCN^-, SO_3^{2-}, CrO_4^{2-}, HCO_3^-, CO_3^{2-}, $NO_2PhSO_3^-$, F^-, Cl^-, and NO_3^{2-} studied, the diffraction of the P3 PCCs seemed to be affected mostly by the presence of SCN^-. Figure S4, Supporting Information, shows the corresponding diffraction spectra.

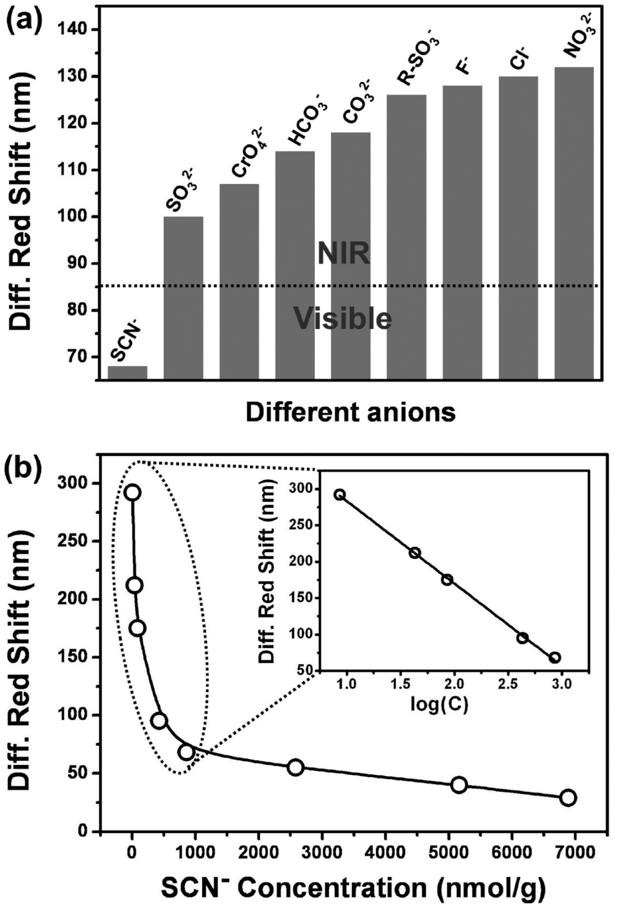


Figure 5. (a) Diffraction peak shift of the P3 PCCs in the presence of the nine anionic ions, as indicated, with the same concentration of 860 nmol/g. The presence of SCN^- suppressed the interaction of water and the hydrogels to the highest degree. (b) The diffraction peak shift of the P3 PCCs in the presence of eight concentrations of SCN^-. The inset is the linear relationship of the PBG shifts in nm versus the logarithm of the low SCN^- concentration range of 8.6 to 860 nmol/g.

Thus, quantitative detection of SCN^- was explored. Figure 5b presents the shift of the diffraction peak position of the P3 PCCs with the addition of 85% of water by weight and eight amounts of SCN^-. It seems that the diffraction-based detection could be quantitative in a large concentration range; for the low concentration range of 8.6 to 860 nmol/g, a linear relationship of the PBG shift versus the logarithm of the low concentration was identified with the correlation coefficients ($R = 0.99796$) and is presented in the inset of Figure 5b. Figure S5, Supporting Information, shows the corresponding diffraction spectra.

Clearly, the presence of SCN^- limited profoundly the swelling behavior of the P3 PCCs. As illustrated in Scheme 1, the water swelling ability of the PCCs of the PS-*co*-PDMAA microspheres is attributed to the formation of hydrogen bonds between the amide side group of DMAA and water. The SCN^- anion is linear in configuration and strong in electrophilicity. Therefore, SCN^- can interact with the PDMAA side chain, suppressing the interaction between water and the PDMAA side chain.

■ CONCLUSIONS

Novel water-tunable PCCs were successfully prepared via centrifugation-induced self-assembly of PS-*co*-PDMAA microspheres with narrow size distribution. With water-tunable PBG, the prepared PCCs exhibited strikingly narrow diffraction bandwidth. Such water tunability was repeatable after centrifugation. Also, our PCCs exhibited brilliant composition dependent color, and the water-induced color change was visible to the naked eye. The maximum change of the diffraction peak could be larger than 500 nm with FWHM smaller than 40 nm. The detection of SCN^- was found to be sensitive and quantitative, with the detection limit as low as 8.6 nmol/g. A detection mechanism was proposed; namely, the interaction between SCN^- and the PDMAA side chain suppressed the interaction between the PDMAA side chain and water molecules. We envision that our PS-*co*-PDMAA PCCs are promising for the fabrication of low-cost sensors based on diffraction.

■ ASSOCIATED CONTENT

Supporting Information

Tables including synthetic parameters of P1, P2, and P3 PS-*co*-PDMAA microspheres and elemental analysis of P1, P2, and P3; SEM and TEM images; dynamic light scattering study; FTIR and ^{1}H NMR spectra; AFM images; diffraction spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 1-613-993-9273 (K.Y.); 86-431-8516-8498 (Q.L.). E-mail: kui.yu@nrc.ca (K.Y.); linquan@jlu.edu.cn (Q.L.).

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Yablonovitch, E. *Phys. Rev. Lett.* **1987**, *58*, 2059−2062.
(2) John, S. *Phys. Rev. Lett.* **1987**, *58*, 2486−2489.
(3) Richard, L. R.; Chirs, S. *Nature* **2000**, *408*, 653−655.
(4) Ibanescu, M.; Fink, Y.; Fan, S.; Thomas, E. L.; Joannopoulos, J. D. *Science* **2000**, *289*, 415−419.
(5) Cregan, R. F.; Mangan, B. J.; Knight, J. C.; Birks, T. A.; Russell, P. S. J.; Roberts, P. J.; Allan, D. C. *Science* **1999**, *285*, 1537−1539.
(6) Hu, X. B.; Li, G. T.; Huang, D.; Zhang, J.; Qiu, Y. *Adv. Mater.* **2007**, *19*, 4327−4332.
(7) Hu, X. B.; Huang, J.; Zhang, W. X.; Li, M. H.; Tao, C. A.; Li, G. T. *Adv. Mater.* **2008**, *20*, 4074−4078.
(8) Holtz, J. H.; Asher, S. A. *Nature* **1997**, *389*, 829−832.
(9) Muscatello, M. M. W.; Stunja, L. E.; Asher, S. A. *Anal. Chem.* **2009**, *81*, 4978−4986.
(10) Xu, X. L.; Goponenko, A. V.; Asher, S. A. *J. Am. Chem. Soc.* **2008**, *130*, 3113−3119.
(11) Zhao, Y. J.; Zhao, X. W.; Gu, Z. Z. *Adv. Funct. Mater.* **2010**, *20*, 2970−2988.
(12) Li, M. Z.; He, F.; Liao, Q.; Liu, J.; Xu, L.; Jiang, L.; Song, Y. L.; Wang, S.; Zhu, D. B. *Angew. Chem., Int. Ed.* **2008**, *47*, 7258−7262.
(13) Burgess, B.; Mishchenko, L.; Hatton, B. D.; Kolle, M.; Loncar, M.; Aizenberg, J. *J. Am. Chem. Soc.* **2011**, *133*, 12430−12432.
(14) Zhao, Y. J.; Zhao, X. W.; Hu, J.; Li, J.; Xu, W. Y.; Gu, Z. Z. *Angew. Chem., Int. Ed.* **2009**, *48*, 7350−7352.
(15) Zhao, Y. J.; Xie, Z. Y.; Gu, H. C.; Zhu, C.; Gu, Z. Z. *Chem. Soc. Rev.* **2012**, *41*, 3297−3317.
(16) Holtz, J. H.; Holtz, J. S. W.; Munro, C. H.; Asher, S. A. *Anal. Chem.* **1998**, *70*, 780−791.
(17) Ozin, G. A.; Arsenault, A. C. *Mater. Today* **2008**, *11*, 44−51.
(18) Moon, J. H.; Yang, S. *Chem. Rev.* **2010**, *110*, 547−574.
(19) Aguirre, C. I.; Reguera, E.; Stein, A. *Adv. Funct. Mater.* **2010**, *20*, 2565−2578.
(20) Ge, J. P.; Yin, Y. D. *Angew. Chem., Int. Ed.* **2011**, *50*, 1492−1522.
(21) Mihi, A.; Zhang, C. J.; Braun, P. V. *Angew. Chem., Int. Ed.* **2011**, *50*, 5712−5715.
(22) Busch, K.; John, S. *Phys. Rev. Lett.* **1999**, *83*, 967−970.
(23) Kim, S. H.; Jeong, W. C.; Hwang, H.; Yang, S. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 11649−11653.
(24) Arsenault, C.; Clark, T. J.; Freymann, G. V.; Cademartiri, L.; Sapienza, R.; Bertolotti, J.; Vekris, E.; Wong, S.; Kitaev, V.; Manners, I.; Wang, R. Z.; John, S.; Wiersma, D.; Ozin, G. A. *Nat. Mater.* **2006**, *5*, 179−184.
(25) Park, H. G.; Kim, S. H.; Kwon, S. H.; Ju, Y. G.; Yang, J. K.; Baek, J. H.; Kim, S. B.; Lee, Y. H. *Science* **2004**, *305*, 1444−1447.
(26) Puzzo, D. P.; Arsenault, A. C.; Manners, I.; Ozin, G. A. *Angew. Chem., Int. Ed.* **2009**, *48*, 943−947.
(27) Zhang, J. H.; Yang, B. *Adv. Funct. Mater.* **2010**, *20*, 3411−3424.
(28) Huang, Y.; Zhou, J. M.; Su, B.; Shi, L.; Wang, J. X.; Chen, S. R.; Wang, L. B.; Zi, J.; Song, Y. L.; Jiang, L. *J. Am. Chem. Soc.* **2012**, *134*, 17053−17058.
(29) Fleischhaker, F.; Arsenault, A. C.; Kitaev, V.; Peiris, F. C.; Freymann, G. V.; Manners, I.; Zentel, R.; Ozin, G. A. *J. Am. Chem. Soc.* **2005**, *127*, 9318−9319.
(30) Ge, J. P.; Lee, H.; He, L.; Kim, J.; Lu, Z.; Kim, H.; Goebl, J.; Kwon, S.; Yin, Y. D. *J. Am. Chem. Soc.* **2009**, *131*, 15687−15694.
(31) Asher, S. A.; Alexeev, V. L.; Goponenko, A. V.; Sharma, A. C.; Lednev, I. K.; Wilcox, C. S.; Finegold, D. N. *J. Am. Chem. Soc.* **2003**, *125*, 3322−3329.
(32) Arsenault, C.; Puzzo, D. P.; Manners, I.; Ozin, G. A. *Nat. Photonics* **2007**, *1*, 468−472.
(33) Lee, K.; Asher, S. A. *J. Am. Chem. Soc.* **2000**, *122*, 9534−9537.
(34) Alexeev, V. L.; Sharma, A. C.; Goponenko, A. V.; Das, S.; Lednev, I. K.; Wilcox, C. S.; Finegold, D. N.; Asher, S. A. *Anal. Chem.* **2003**, *75*, 2316−2323.
(35) Kim, H.; Ge, J.; Kim, J.; Choi, S. E.; Lee, H.; Park, W.; Yin, Y.; Kwon, S. *Nat. Photonics* **2009**, *3*, 534−540.
(36) Wang, J. X.; Zhang, Y. Z.; Wang, S. T.; Song, Y. L.; Jiang, L. *Acc. Chem. Res.* **2011**, *44*, 405−415.
(37) Matsubara, K.; Watanabe, M.; Takeoka, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 1688−1692.
(38) Barry, R. A.; Wiltzius, P. *Langmuir* **2006**, *22*, 1369−1374.
(39) Li, H. L.; Wang, J. X.; Yang, L. M.; Song, Y. L. *Adv. Funct. Mater.* **2008**, *18*, 3258−3264.
(40) Huang, J.; Tao, C. A.; An, Q.; Lin, C. X.; Li, X. S.; Xu, D.; Wu, Y. G.; Li, X. G.; Shen, D. Z.; Li, G. T. *Chem. Commun.* **2010**, *46*, 4103−4105.
(41) Kim, E.; Kim, S. Y.; Jo, G.; Kim, S.; Park, M. J. *ACS Appl. Mater. Interfaces* **2012**, *4*, 5179−5187.
(42) Shim, T. S.; Kim, S. H.; Sim, J. Y.; Lim, J. M.; Yang, S. M. *Adv. Mater.* **2010**, *22*, 4494−4498.
(43) Weissman, J. M.; Sunkara, H. B.; Tse, A. S.; Asher, S. A. *Science* **1996**, *274*, 959−960.
(44) Debord, J. D.; Lyon, L. A. *J. Phys. Chem. B* **2000**, *104*, 6327−6331.
(45) Debord, J. D.; Eustis, S.; Debord, S. B.; Lofye, M. T.; Lyon, L. A. *Adv. Mater.* **2002**, *14*, 658−662.
(46) Sorrell, D.; Serpe, M. J. *Adv. Mater.* **2011**, *23*, 4088−4092.
(47) Zulian, L.; Emilitri, E.; Scavia, G.; Botta, C.; Colombo, M.; Desri, S. *ACS Appl. Mater. Interfaces* **2012**, *4*, 6071−6079.
(48) Lü, C. L.; Cheng, Y. R.; Liu, Y. F.; Liu, F.; Yang, B. *Adv. Mater.* **2006**, *18*, 1188−1192.

(49) Lin, Z.; Cheng, Y. R.; Lü, H.; Zhang, L.; Yang, B. *Polymer* **2010**, *51*, 5425−5431.
(50) Zhang, G. Y.; Zhang, H.; Zhang, X. R.; Zhu, S. J.; Zhang, L.; Meng, Q. N.; Wang, M. Y.; Li, Y. F.; Yang, B. *J. Mater. Chem.* **2012**, *22*, 21218−21224.
(51) Carlsson, L.; Rose, S.; Hourdet, D.; Marcellan, A. *Soft Matter* **2010**, *6*, 3619−3631.
(52) Banik, S. J.; Fernandes, N. J.; Thomas, P. C.; Raghavan, S. R. *Macromolecules* **2012**, *45*, 5712−5717.
(53) Xiao, X. C.; Chu, L. Y.; Chen, W. M.; Wang, S.; Xie, R. *Langmuir* **2004**, *20*, 5247−5253.
(54) Jiang, Y. N.; Yang, X. D.; Ma, C.; Wang, C. X.; Li, H.; Dong, F. X.; Zhai, X. M.; Yu, K.; Lin, Q.; Yang, B. *Small* **2010**, *6* (23), 2673−2677.
(55) Frank, R. S.; Downey, J. S.; Yu, K.; Stöver, D. H. *Macromolecules* **2002**, *35*, 2728−2735.
(56) Meng, Q. B.; Li, Z. Y.; Li, G.; Zhu, X. X. *Macromol. Rapid Commun.* **2007**, *28*, 1613−1618.
(57) Hellweg, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 6777−6778.
(58) Asher, S. A.; Holtz, J.; Liu, L.; Wu, Z. *J. Am. Chem. Soc.* **1994**, *116*, 4997−4998.
(59) Diego, A.; Simone, D.; Guido, P.; Katia, S.; Michele, L.; Luca, B.; Luca, F.; Matteo, G.; Luca, B.; Emanuele, E.; Davide, C. *Polym. Int.* **2012**, *61*, 1294−1301.
(60) Wang, J. Y.; Cao, Y.; Feng, Y.; Yin, F.; Gao, J. P. *Adv. Mater.* **2007**, *19*, 3865−3871.
(61) Bandtsen, A. B.; Hansen, E. H. *Analyst* **1991**, *116*, 647−651.
(62) Bjorck, L.; Claesson, O.; Schulthess, W. *Milchwissenschaft* **1979**, *34*, 726−729.
(63) Staden, J. F. V.; Botha, A. *Anal. Chim. Acta* **2000**, *403*, 279−286.
(64) Li, L.; Wang, A.; He, P.; Fang, Y. *Fresenius' J. Anal. Chem.* **2000**, *367*, 649−654.

■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on February 28, 2013, with an incorrect symbol designation in the caption of Figure 4. The corrected version was reposted on March 15, 2013.