ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

Core–Shell Polymeric Microcapsules with Superior Thermal and Solvent Stability

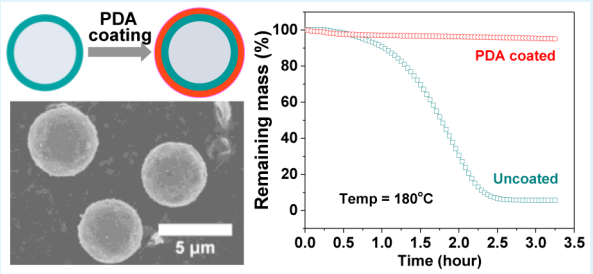
Sen Kang,[†] Marta Baginska,[‡,§] Scott R. White,[‡] and Nancy R. Sottos*[,†]

[†]Beckman Institute for Advanced Science and Technology, Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States

[‡]Beckman Institute for Advanced Science and Technology, Department of Aerospace Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States

Supporting Information

ABSTRACT: A protective polydopamine (PDA) coating is applied to core–shell microcapsule surfaces by the polymerization of dopamine monomers. A neutral aqueous solution and the addition of an oxidant (i.e., ammonium persulfate) are crucial for microcapsule survival and the initiation of PDA polymerization, respectively. The resulting PDA coating is a dense and uniform layer approximately 50 nm thick. The PDA protective coating significantly increases capsule stability at an elevated temperature (180 °C) and in a variety of organic solvents and acidic/basic solutions that otherwise lead to deflation and loss of the core content of uncoated microcapsules.



KEYWORDS: *microcapsules, polydopamine, thermal stability, solvent stability*

INTRODUCTION

Microcapsules containing functional core contents are used in a wide range of applications, including self-healing materials, drug delivery, food additives, and paints.[1−3] Upon exposure to external stimuli, the microcapsule shell wall ruptures or disintegrates and the core content is delivered to fulfill a specific function.[4−6] For many applications, the microcapsule must remain stable for an extended period of time before delivering its payload.[7] Any loss of core prior to exposure to stimuli, during storage, manufacturing, or service, will lead to weakened function of encapsulated systems.[8]

Harsh environments, such as elevated temperatures or strong solvents, can degrade the microcapsule shell wall and accelerate diffusion of the core through the shell wall because of the chemical gradients. In self-healing polymers, high processing temperatures (>100 °C) can cause diffusion of the core to the host matrix, reducing self-healing capability.[9] Additionally, wet processing in polymeric composite fabrication often involves strong solvents that can degrade the capsule shell wall.[10]

Li et al. introduced double-layer core–shell microcapsules by condensing urea-formaldehyde (UF) resin on as-prepared polyurethane (PU) microcapsule surfaces.[11] Subsequently, Caruso et al. developed an improved single-batch process to prepare PU/UF double-layer microcapsules.[12] The microcapsules showed moderate core loss at an elevated temperature (~10 wt % loss at 180 °C for 2 h). Jackson et al. reported a technique to coat a 20−40 nm thick silica layer on microcapsule surfaces for improved environmental stability.[13]

In this paper, we evaluate the ability of a polydopamine (PDA) coating to protect microcapsules and improve capsule stability. Inspired by the adhesive proteins in mussels where the coexistence of catechol and amine groups is crucial for strong adhesion properties, dopamine is a powerful building block that contains both catechol and amine moieties. As a result, the polymeric form of dopamine, PDA, shows strong adhesion on virtually all types of surfaces.[14,15] Under basic conditions, dopamine immediately undergoes polymerization and deposits on the target surface as PDA.[16] Though the detailed structure of PDA remains elusive, recent investigations have shown that hydrogen bonding and $\pi-\pi$ stacking make PDA a dense membrane with remarkable stability.[17]

EXPERIMENTAL SECTION

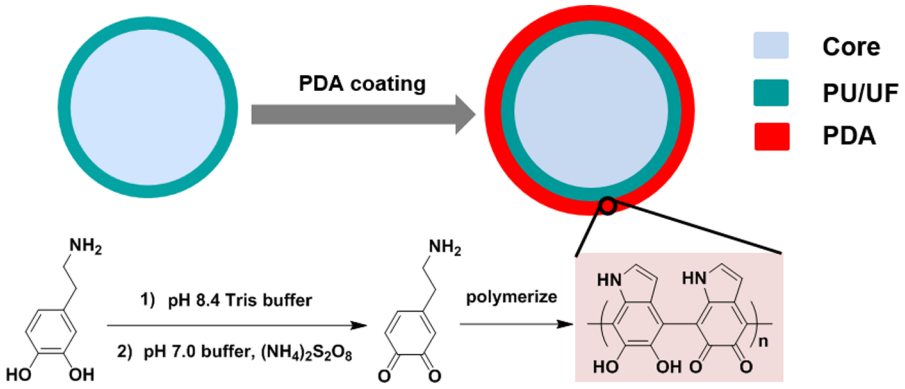
Materials. *o*-Dichlorobenzene (*o*-DCB), urea, ammonium chloride, resorcinol, a formalin solution [37% (w/v)], ammonium persulfate, dopamine hydrochloride, sodium phosphate monobasic monohydrate, sodium citrate dihydrate, tris(hydroxymethyl)aminomethane (TRIS), and sodium hydroxide were used as received from Sigma-Aldrich. The commercial polyurethane (PU) prepolymer, Desmodur L75, was obtained from Bayer Material Science and used as received. Ethylene-maleic anhydride (EMA) copolymer (Zemac-400) powder (~400 kDa) was from Vertellus and used as a 1.25 wt % aqueous solution.

Preparation of Microcapsules. The encapsulation procedure was adapted from an established PU/UF double-shell wall method.[12] Urea (0.9 g), ammonium chloride (0.2 g), and resorcinol (0.09 g) were dissolved in a 1.25 wt % EMA aqueous solution (60 mL). *o*-DCB (10 mL) that contains Desmodur L75 (0.33 g) was subsequently added to

Received: March 13, 2015
Accepted: April 29, 2015
Published: April 29, 2015

DOI: 10.1021/acsami.5b02169
ACS Appl. Mater. Interfaces 2015, 7, 10952−10956

Scheme 1. Polymerization of Dopamine and Deposition of PDA on Core–Shell Microcapsule Surfaces under Two Different Conditions[a]



[a](1) In the pH 8.4 buffer solution in the presence of TRIS. (2) In the pH 7.0 buffer solution in the presence of ammonium persulfate.

the aqueous phase. A fine emulsion was formed after homogenization of the mixture for 3 min (Omni GLH). The emulsion was mechanically stirred at 800 rpm. After a formalin solution (2.4 g) had been added, the emulsion was heated to 55 °C and allowed to react for 4 h. Microcapsules were separated by centrifugation and then washed with water three times to remove the residual surfactant and unencapsulated shell wall particles. Free-flowing microcapsules were obtained by freeze-drying.

PDA Coating of Microcapsules. In the first approach, microcapsules (0.2 g) were predispersed in a pH 8.4 buffer solution (10 mL). Dopamine hydrochloride (0.04 g) was then added to the stirring solution. The solution turned brown within 20 min, indicating the polymerization of dopamine. After 1 day, the coated microcapsules were centrifuged, rinsed with water three times, and freeze-dried to obtain free-flowing powder. The pH 8.4 buffer contained 1 M TRIS in deionized water. HCl was used to adjust the pH to 8.4.

In the second approach, microcapsules (0.2 g) were predispersed in a pH 7.0 buffer solution (10 mL). Dopamine (0.04 g) and ammonium persulfate (0.04 g) were then added to the stirring solution. After 1 day, the microcapsules were collected using the same procedure described above. The pH 7.0 buffer solution contained 1 M sodium phosphate monobasic monohydrate and 1 M sodium citrate dihydrate. NaOH was used to adjust the pH to 7.0.

Similarly, PDA polymer was made by adding dopamine (0.04 g) and ammonium persulfate (0.04 g) to the pH 7.0 buffer solution (10 mL) and reacting for 1 day. PDA was centrifuged, rinsed with water three times, and dried under vacuum.

Characterization of Microcapsules. Microcapsule morphology was studied using scanning electron microscopy (SEM) (Hitachi 4800) and transmission electron microscopy (TEM) (Philips CM200). For SEM characterization, the microcapsules were placed on conductive carbon tape and sputter-coated with Au/Pd prior to imaging (accelerating voltage of 10 kV). For the observation of the microcapsule shell wall, dried microcapsules were dispersed in epoxy resin (EPON 828 and 12 wt % DETA). After the epoxy resin was fully cured, the sample was microtomed to expose the shell wall of ruptured microcapsules. TEM was used to characterize the microcapsule shell wall.

The microcapsule shell wall components before and after PDA coating were characterized by Fourier transform infrared spectroscopy (Thermo Nicolet NEXUS 670 FTIR). The microcapsules were ground with a mortar and pestle to allow the release and evaporation of core liquid. Pellet samples were made with potassium bromide and stored under vacuum prior to being tested to eliminate moisture.

Thermal analysis of microcapsules was performed on a Mettler-Toledo thermogravimetric analysis (TGA) 851 instrument. For the dynamic experiments, the microcapsules were heated from 25 to 600 °C, at a heating rate of 10 °C/min, under a nitrogen atmosphere. For the isothermal studies, the microcapsules were heated from 25 to 180 °C (heating rate of 10 °C/min) and then held at 180 °C for 3 h. The mass change was recorded throughout the entire experiment.

Solvent Stability of Microcapsules. For optical observation, uncoated and PDA-coated microcapsules were added to the desired solvents (5 wt % in water, pH 4 buffer solution, pH 10 buffer solution, acetone, ethyl acetate, and chloroform). After 3 days, an aliquot was taken, and the morphology of microcapsules was observed under an optical microscope (Leica DMR optical microscope). In the cases of acetone, ethyl acetate, and chloroform, the images showed the dried microcapsules. In water and pH 4 and 10 buffer solutions, the images showed the dispersed microcapsules in aqueous media.

The ^{1}H NMR method was used to quantify the percent core release of microcapsules in several solvents (acetone, ethyl acetate, and chloroform). Microcapsules (50 mg) were added to the desired solvent (1 g). After 3 days, hexyl acetate (20 mg) was added to the suspension as an internal standard. Subsequently, an aliquot was taken and filtered to remove the microcapsules. The filtered clear liquid was diluted by *d*-chloroform for ^{1}H NMR measurement. The released *o*-DCB concentration was calculated on the basis of the integrated peak ratios of *o*-DCB and hexyl acetate in ^{1}H NMR spectra.

RESULTS AND DISCUSSION

Microcapsules containing *o*-DCB are prepared by a combined *in situ*/interfacial emulsion technique (Experimental Section).[12,18] Two coating conditions with different solution pH values are used to form PDA coatings on microcapsule surfaces (Scheme 1). PDA is commonly prepared by the polymerization of dopamine hydrochloride in a TRIS buffer solution at pH 8.4.[16] The catechol moieties in dopamine are oxidized to quinine and subsequently undergo polymerization to form PDA, accompanied by a color change from transparent to dark brown within 20 min. In the first approach, PDA is coated on microcapsule surfaces in an aqueous solution at pH 8.4. In the second approach, the PDA coating is formed in a neutral aqueous solution at pH 7.0. Although the polymerization of dopamine does not typically occur at neutral pH, here we add ammonium persulfate to oxidize the catechol to quinine and initiate the polymerization.[19]

The deposition of PDA on capsule surfaces is evident from the SEM and TEM images in Figure 1. In contrast to the smooth surface morphology of uncoated microcapsules (Figure 1a), PDA-coated microcapsules have enhanced surface roughness, indicating the deposition of PDA. The microcapsules prepared in basic solution (pH 8.4) have an irregular shape and poor shell wall integrity. Under high-pH conditions, the capsule shell wall deteriorates and leads to the release of *o*-DCB core

DOI: 10.1021/acsami.5b02169
ACS Appl. Mater. Interfaces 2015, 7, 10952–10956

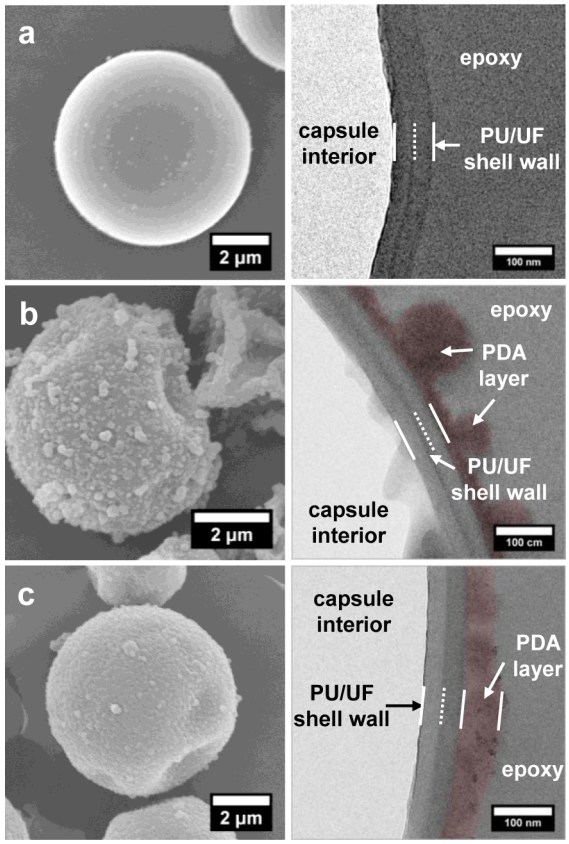


Figure 1. Microcapsule morphologies and shell wall cross sections for different processing conditions. (a) SEM and TEM of the cross section of an uncoated PU/UF microcapsule. (b) SEM and TEM of the cross section of a PDA-coated microcapsule prepared in the pH 8.4 solution. (c) SEM and TEM of the cross section of a PDA-coated microcapsule prepared in the pH 7.0 solution.

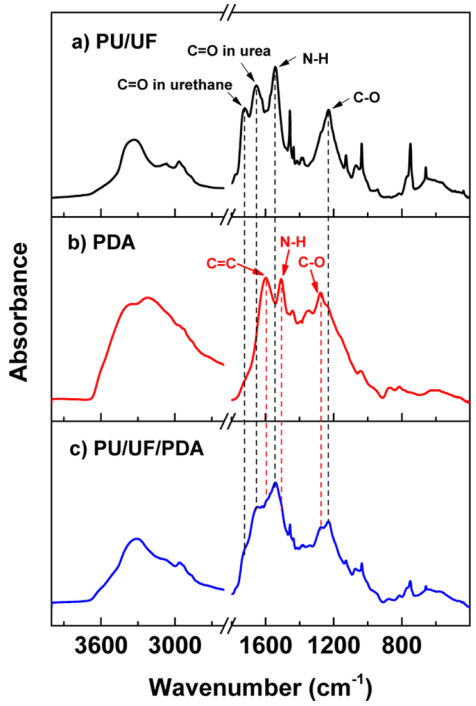


Figure 2. Comparison of FTIR spectra of shell wall materials. (a) PU/UF from ground uncoated microcapsules. (b) PDA synthesized in the pH 7.0 buffer solution. (c) PU/UF/PDA from ground PDA-coated microcapsules. The absorbance peaks in PU/UF/PDA are indicated by the vertical black and red dotted lines corresponding to the absorbance peaks in neat PU/UF and PDA.

into the aqueous media. We hypothesize the core leakage leads to a poor capsule surface for PDA polymerization, resulting in a rough PDA coating and less stable capsules. In great contrast, the microcapsules prepared with the pH 7.0 buffer solution retained their spherical shape and uniform thickness (Figure 1c). The dimple of the capsule was caused by the exposure (~30 s) to the electron beam of the scanning electron microscope. The PDA coating was ~50 nm thick, similar to the thickness of the inner PU/UF layer. Only the PDA-coated microcapsules prepared under neutral pH conditions (pH 7.0) were subject to further characterization studies.

The PDA coating on microcapsules was confirmed by FTIR measurements (Figure 2). The FTIR spectrum of the PDA-coated microcapsule shell wall showed the characteristic absorbance peaks of both PU/UF and PDA polymers. The absorbance peaks of PU/UF/PDA from 1800 to 1400 cm^{-1} are the superpositions of the absorbance peaks of PU/UF at 1723, 1653, 1543, and 1231 cm^{-1} (C═O stretching from urethane, C═O stretching from urea, N−H scissoring, and C−O stretching, respectively) and the absorbance peaks of PDA at 1510, 1600, and 1274 cm^{-1} (N−H scissoring, C═C stretching from the indole ring, and C−O stretching from phenolic moieties, respectively).[20,21] The broad peak of PU/UF/PDA from 2700 to 3700 cm^{-1} is an overlap of the peaks from PU/UF (O−H stretching, N−H stretching, and aromatic and aliphatic C−H stretching) and PDA (hydrogen bonding, O−H stretching, N−H stretching, and aromatic and aliphatic C−H stretching) spectra.

The thermal stability of microcapsules was evaluated by TGA under dynamic and isothermal conditions. In the dynamic experiment (Figure 3a), weight loss of uncoated microcapsules was initiated at 225 °C because of the rupture of the shell wall and evaporation of the *o*-DCB core. For PDA-coated microcapsules, the onset weight loss temperature increased by ~20 to 245 °C. Above 200 °C, *o*-DCB (bp 180 °C) is volatile. We hypothesized that the PDA shell wall was able to hold a vapor pressure of *o*-DCB higher than that held by the PU/UF shell wall, postponing the microcapsule rupture temperature by 20 °C. At 600 °C, we observed ~10 wt % residue mass for PDA-coated microcapsules in contrast to the complete decomposition of uncoated PU/UF capsules. This 10 wt % residue mass was from PDA coating, consistent with the initial ratio of capsules to PDA monomers (5:1) for the coating process and the ~60 wt % remaining mass of the plain PDA polymer at 600 °C (Figure S1 of the Supporting Information). Thermal stability was further studied by isothermal TGA of microcapsules at 180 °C for 3 h (Figure 3b). The weight loss for uncoated microcapsules was 94.4 wt % at 180 °C, leaving only the microcapsule shell wall. The PDA-coated microcapsules only lost 3.7% of their weight, showing good core retention ability at high temperatures.

To evaluate the stability in solvent, we soaked the microcapsules in different organic solvents and aqueous solutions with different pH levels at room temperature. Optical images of the microcapsules after they had been immersed for 3 days were taken (Figure 4). In aqueous systems, both uncoated and PDA-coated microcapsules showed good survival in acidic (pH 4) and neutral solutions. However, uncoated micro-

DOI: 10.1021/acsami.5b02169
ACS Appl. Mater. Interfaces 2015, 7, 10952−10956

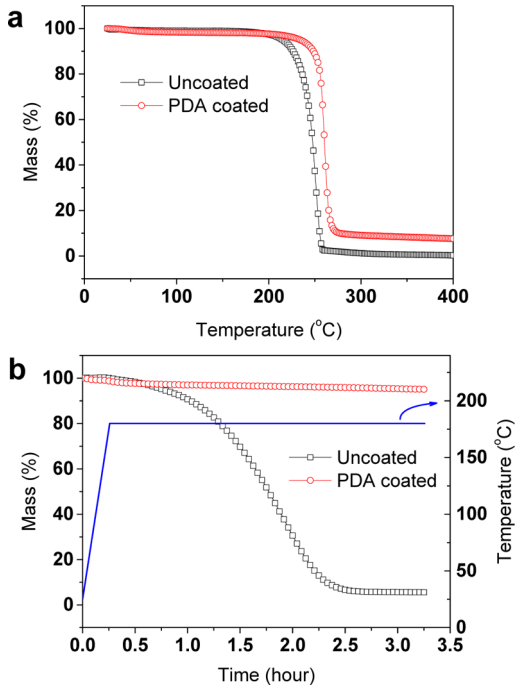


Figure 3. Thermal stability of uncoated and PDA-coated microcapsules. TGA results for (a) dynamic scanning (25−400 °C, 10 °C/min) and (b) isothermal conditions (180 °C, 3 h). The blue line shows the temperature profile.

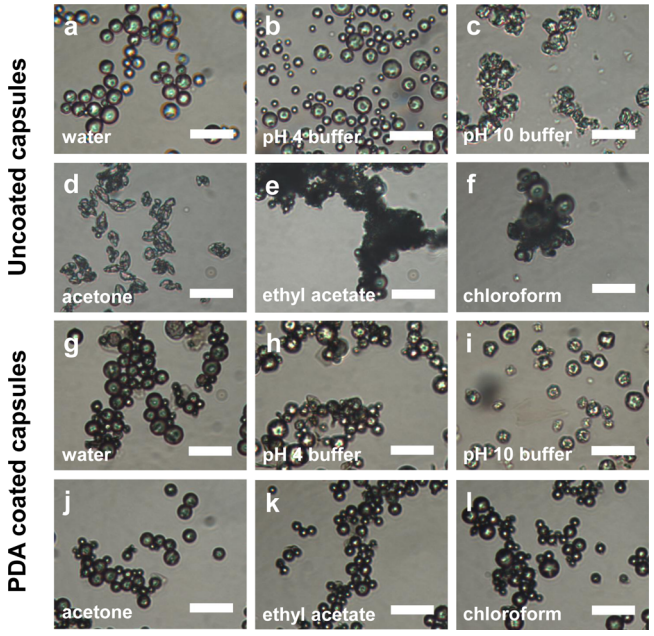


Figure 4. Microcapsule stability under various solvent conditions. Optical images taken after immersion of (a−c) uncoated microcapsules and (g−i) PDA-coated microcapsules in neutral (pH 7.0), acidic (pH 4.0), and basic (pH 10.0) buffer solutions, (d−f) uncoated microcapsules, and (j−l) PDA-coated microcapsules immersed in different solvents for 3 days. The scale bar is 20 μm for all images.

capsules deflated in the pH 10 solution, while PDA-coated microcapsules retained the majority of the core. In organic solvents (acetone, ethyl acetate, and chloroform), uncoated microcapsules were not able to maintain the core and significant deflation and agglomeration were observed (Figure 4g−i). In contrast, the PDA-coated microcapsules remained dispersed and spherical, suggesting good solvent stability.

The percent of core release of the microcapsules in different solvents after immersion for 3 days was quantified by ^{1}H NMR (Figure 5). PDA-coated capsules retained >90% of the *o*-DCB

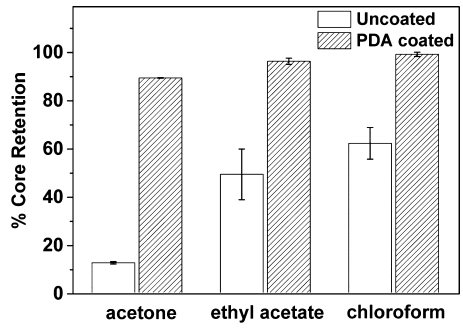


Figure 5. Weight percent of *o*-DCB retention in microcapsules after immersion for 3 days in organic solvents measured by ^{1}H NMR.

core in acetone, ethyl acetate, and chloroform, while the uncoated capsules lost from 40 to 90% of core content depending on the solvent.

CONCLUSION

Microcapsules with superior thermal and solvent stability were prepared by coating core−shell microcapsules with a PDA polymer film. The PDA coating effectively limited the diffusion of the core liquid through the microcapsule shell wall at an elevated temperature (180 °C). The reduced permeability of the capsule shell wall was also observed in common organic solvents as well as in a basic aqueous solution. The PDA protective coating served as an effective barrier for *o*-DCB core diffusion. The superior thermal stability and the superior solvent stability of the PDA-coated microcapsules make them promising candidates for self-healing polymers and composites cured at elevated temperatures, and also for a variety of applications for which exceptional capsule stability is required.

ASSOCIATED CONTENT

Supporting Information

TGA of the PDA polymer synthesized in the pH 7.0 buffer solution (Figure S1) and TGA of PDA-coated capsules coated in the pH 8.4 buffer solution (Figure S2). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b02169.

AUTHOR INFORMATION

Corresponding Author

*E-mail: n-sottos@illinois.edu.

Present Address

§M.B.: The Boeing Co., 5400 International Blvd., MC 7819-1155, North Charleston, SC 29418.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported as part of the Center for Electrochemical Energy Science, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of

DOI: 10.1021/acsami.5b02169
ACS Appl. Mater. Interfaces 2015, 7, 10952−10956

Science, Basic Energy Sciences. We thank Amanda Jones for helpful discussions.

REFERENCES

(1) Blaiszik, B. J.; Kramer, S. L. B.; Olugebefola, S. C.; Moore, J. S.; Sottos, N. R.; White, S. R. Self-Healing Polymers and Composites. *Annu. Rev. Mater. Res.* **2010**, *40*, 179−211.
(2) White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R.; Sriram, S. R.; Brown, E. N.; Viswanathan, S. Autonomous Healing of Polymer Composites. *Nature* **2001**, *409*, 794−797.
(3) Esser-Kahn, A. P.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. Triggered Release from Polymer Capsules. *Macromolecules* **2011**, *44*, 5539−5553.
(4) Jones, A. R.; Blaiszik, B. J.; White, S. R.; Sottos, N. R. Full Recovery of Fiber/Matrix Interfacial Bond Strength using a Microencapsulated Solvent-Based Healing System. *Compos. Sci. Technol.* **2013**, *79*, 1−7.
(5) Cho, S. H.; White, S. R.; Braun, P. V. Self-Healing Polymer Coatings. *Adv. Mater.* **2009**, *21*, 645−649.
(6) Yuan, Y. C.; Rong, M. Z.; Zhang, M. Q.; Chen, J.; Yang, G. C.; Li, X. M. Self-Healing Polymeric Materials Using Epoxy/Mercaptan as the Healant. *Macromolecules* **2008**, *41*, 5197−5202.
(7) Patel, A. J.; Sottos, N. R.; Wetzel, E. D.; White, S. R. Autonomic Healing of Low-Velocity Impact Damage in Fiber-Reinforced Composites. *Composites, Part A* **2010**, *41*, 360−368.
(8) Jin, H.; Mangun, C. L.; Stradley, D. S.; Moore, J. S.; Sottos, N. R.; White, S. R. Self-Healing Thermoset using Encapsulated Epoxy-Amine Healing Chemistry. *Polymer* **2012**, *53*, 581−587.
(9) Jin, H.; Mangun, C. L.; Griffin, A. S.; Moore, J. S.; Sottos, N. R.; White, S. R. Thermally Stable Autonomic Healing in Epoxy using a Dual-Microcapsule System. *Adv. Mater. (Weinheim, Ger.)* **2014**, *26*, 282−287.
(10) Yuan, L.; Gu, A.; Liang, G. Preparation and Properties of Poly(urea−formaldehyde) Microcapsules Filled with Epoxy Resins. *Mater. Chem. Phys.* **2008**, *110*, 417−425.
(11) Li, G.; Feng, Y.; Gao, P.; Li, X. Preparation of Mono-Dispersed Polyurea-Urea Formaldehyde Double Layered Microcapsules. *Polym. Bull.* **2008**, *60*, 725−731.
(12) Caruso, M. M.; Blaiszik, B. J.; Jin, H.; Schelkopf, S. R.; Stradley, D. S.; Sottos, N. R.; White, S. R.; Moore, J. S. Robust, Double-Walled Microcapsules for Self-Healing Polymeric Materials. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1195−1199.
(13) Jackson, A. C.; Bartelt, J. A.; Marczewski, K.; Sottos, N. R.; Braun, P. V. Silica-Protected Micron and Sub-Micron Capsules and Particles for Self-Healing at the Microscale. *Macromol. Rapid Commun.* **2011**, *32*, 82−87.
(14) Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B. Mussel-Inspired Surface Chemistry for Multifunctional Coatings. *Science* **2007**, *318*, 426−430.
(15) Ryou, M. H.; Kim, J.; Lee, I.; Kim, S.; Jeong, Y. K.; Hong, S.; Ryu, J. H.; Kim, T.-S.; Park, J. K.; Lee, H.; Choi, J. W. Mussel-Inspired Adhesive Binders for High-Performance Silicon Nanoparticle Anodes in Lithium-Ion Batteries. *Adv. Mater.* **2013**, *25*, 1571−1576.
(16) Dreyer, D. R.; Miller, D. J.; Freeman, B. D.; Paul, D. R.; Bielawski, C. W. Perspectives on Poly(dopamine). *Chem. Sci.* **2013**, *4*, 3796.
(17) Dreyer, D. R.; Miller, D. J.; Freeman, B. D.; Paul, D. R.; Bielawski, C. W. Elucidating the Structure of Poly(dopamine). *Langmuir* **2012**, *28*, 6428−6435.
(18) Blaiszik, B. J.; Caruso, M. M.; McIlroy, D. A.; Moore, J. S.; White, S. R.; Sottos, N. R. Microcapsules Filled with Reactive Solutions for Self-Healing Materials. *Polymer* **2009**, *50*, 990−997.
(19) Wei, Q.; Zhang, F.; Li, J.; Li, B.; Zhao, C. Oxidant-Induced Dopamine Polymerization for Multifunctional Coatings. *Polym. Chem.* **2010**, *1*, 1430−1433.
(20) Luo, R.; Tang, L.; Wang, J.; Zhao, Y.; Tu, Q.; Weng, Y.; Shen, R.; Huang, N. Improved Immobilization of Biomolecules to Quinone-Rich Polydopamine for Efficient Surface Functionalization. *Colloids Surf., B* **2013**, *106*, 66−73.
(21) Müller, M.; Keßler, B. Deposition from Dopamine Solutions at Ge Substrates: An in Situ ATR-FTIR Study. *Langmuir* **2011**, *27*, 12499−12505.

DOI: 10.1021/acsami.5b02169
ACS Appl. Mater. Interfaces 2015, 7, 10952−10956