Smart Materials

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Water-Enabled Self-Healing of Polyelectrolyte Multilayer Coatings**

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Self-healing materials have the ability to repair damage caused by mechanical usage over time. The demand for self-healing materials is rapidly growing because they may have longer lifetimes and lower production costs.[1] Among various self-healing materials, self-healing coatings capable of endowing the underlying substrates with desired properties and protecting the substrates against damage or corrosion are indispensable in daily life.[2] Generally, self-healing of materials can be achieved in different ways. One frequently employed approach for extrinsic self-healing materials is the release of healing agents compartmentalized in microcapsules[2c,3] or microvascular networks[2b,4] by crack propagation. Intrinsic self-healing materials achieve repair through the inherent reversibility of chemical bonds and physical interactions between the damaged interfaces, for examples, reversible covalent bonds, noncovalent bonds, and molecular diffusion.[1e] Interest in intrinsic self-healing materials has been growing,[5] because they require no incorporation of healing agents; this avoids many of the intractable problems associated with healing agents, such as complicated pre-embedding processes, compatibility, and controlled and sustained release.[1e,f,3a] However, the fabrication of intrinsic self-healing materials, especially those with satisfactory mechanical properties and capable of autonomic repair of severe damage, remains an ongoing challenge. The fabrication of intrinsic self-healing coatings is even more challenging than production of the corresponding bulk healing materials, because strong binding from the underlying substrates restricts the migration of the molecular components across damaged areas, and therefore restricts healing of the coatings.

Layer-by-layer (LbL) assembly, which involves alternate deposition of species with complementary chemical interactions, is a substrate-independent method for the fabrication of various kinds of coatings with controlled properties.[6] Recent studies have shown that LbL assembly is promising for fabricating extrinsic self-healing coatings.[7] In a previous publication, we observed that grooves on polyelectrolyte multilayer (PEM) films created by room-temperature imprinting using patterned molds could be erased by swelling the films in water.[8] This observation suggests that defects such as pits on PEM films caused by pressing can be healed in water. Lyon and South first demonstrated the concept that LbL-assembled hydrogel thin films deposited on poly(dimethylsiloxane) elastomers could undergo rapid healing of micrometer-sized defects when exposed to water.[9] Despite these achievements, LbL assembly for the fabrication of intrinsic self-healing coatings is still in its infancy, because the self-healing mechanism is unclear, and preparation by LbL assembly of robust PEM coatings capable of healing severe damage is still a challenge. Herein, we present a facile exponential LbL assembly method for the rapid fabrication of intrinsic self-healing PEM coatings. The as-prepared PEM coatings are mechanically robust under ambient conditions, but can be softened to flow and bring the damaged surfaces into intimate contact in the presence of water. Autonomic healing of severe damage on the coatings can therefore be realized by simply immersing the coatings in water or spraying water on the coatings. The self-healing mechanism and the fundamental parameters governing the healing ability of the coatings are clarified.

PEM coatings with autonomic repairing abilities are fabricated by alternately dipping substrates in aqueous solutions of branched poly(ethylenimine) (bPEI) ($M_w \approx 750\,000$, 4 mg mL^{-1}, pH 10.5) and poly(acrylic acid) (PAA) ($M_w \approx 450\,000$, 4 mg mL^{-1}, pH 3) for 15 min each time, with intermediate washing with water to remove physically adsorbed polyelectrolytes. PEM coatings with n deposition cycles are denoted as (bPEI10.5/PAA3)*n, where the pH values of bPEI and PAA are given next to their names. The thicknesses of bPEI10.5/PAA3 coatings with different numbers of deposition cycles, determined from their corresponding cross-sectional scanning electron microscopy (SEM) images, are shown in Figure 1 a. The bPEI10.5/PAA3 coatings exhibit a typical exponential deposition behavior in the initial 15 deposition cycles, and thereafter a rapid linear growth with an increment of approximately 1.8 μm per deposition cycle. The bPEI10.5/PAA3 coatings grow rapidly to reach a thickness of (34.1 ± 3.3) μm after 30 deposition cycles. The LbL deposition of bPEI/PAA coatings is largely dependent on the pH of the polyelectrolyte dipping solutions. As shown in Figure 1 b, the growth rate of (bPEI6.5/PAA3)*n coatings significantly decreases when the pH of the bPEI dipping solution decreases from 10.5 to 6.5. A (bPEI6.5/PAA3)*300 coating has a thickness of (29.4 ± 2.9) μm. bPEI conjugated with fluorescein isothiocyanate (FITC) (bPEI-FITC) and PAA conjugated with lucifer yellow cadaverine (LYC) (PAA-LYC) were deposited as the top layers of bPEI/PAA coatings, and their diffusion into the coatings was characterized by confocal laser scanning microscopy (CLSM) (Figure 1 c–f). It can be clearly seen that PAA can diffuse throughout the entire (bPEI10.5/PAA3)*30.5 and (bPEI6.5/PAA3)*300.5 coatings, but bPEI has a much deeper diffusion depth in the

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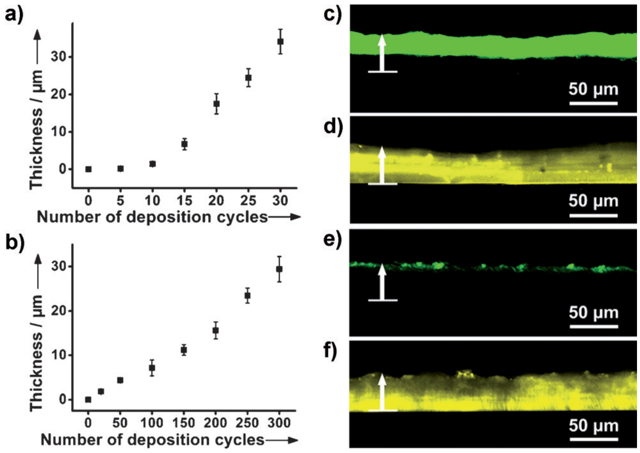

Figure 1. a,b) Thicknesses of bPEI10.5/PAA3 (a) and bPEI6.5/PAA3 (b) coatings as a function of the number of deposition cycles. c–f) Characterization of dye-labeled polyelectrolyte diffusion in bPEI10.5/PAA3 (c,d) and bPEI6.5/PAA3 (e,f) coatings by laser scanning confocal microscopy. c,e) (bPEI10.5/PAA3)*30 (c) and (bPEI6.5/PAA3)*300 (e) coatings with a top layer of bPEI-FITC. d,f) (bPEI10.5/PAA3)*30.5 (d) and (bPEI6.5/PAA3)*300.5 (f) coatings with a top layer of PAA-LYC. The arrows indicate the actual coating thickness.

(bPEI10.5/PAA3)*30 coating than in the (bPEI6.5/PAA3)*300 coating. The rapid exponential LbL deposition of the bPEI10.5/PAA3 coatings is ascribed to "in-and-out" diffusion of bPEI and PAA during the coating fabrication process. The "in-and-out" diffusion mechanism for the exponential growth of LbL-assembled polyelectrolyte films was first proposed by Picart, Lavalle, and co-workers,[10] and further verified by others.[11] The ionic charge density of bPEI6.5 is higher than that of bPEI10.5 because bPEI is easily protonated in solutions of low pH. Therefore, the bPEI6.5/PAA3 coatings are believed to have a higher ionic cross-linking density than bPEI10.5/PAA3 coatings have. The configuration adopted by bPEI6.5 in the dipping solution is more extended than that adopted by bPEI10.5. As a result, the diffusion of bPEI6.5 in bPEI6.5/PAA3 coatings is partially blocked, which explains why the deposition of bPEI6.5/PAA3 coatings is slower than that of bPEI10.5/PAA3 coatings. CLSM images also demonstrate that the diffusion of bPEI is more sensitive than the diffusion of linear PAA to the pH of the dipping solution and structure of the bPEI/PAA coatings.

The self-healing abilities of the as-prepared bPEI/PAA coatings are largely dependent on their structures, which are governed by the pH of the polyelectrolyte dipping solutions. The scanning electron microscope (SEM) images in Figure 2a–f show the self-healing process of a damaged (bPEI10.5/PAA3)*30 coating on a silicon substrate. The (bPEI10.5/PAA3)*30 coating is compact and has intimate contact with the underlying silicon substrate. Cuts roughly 50 μm in width, which penetrated to the silicon surface, were made using a scalpel (Figure 2a,b). Obvious healing of the cuts was observed after the damaged coating was immersed in water for 10 s (Figure 2c,d). However, complete healing of the cuts usually takes about 5 min, as indicated in Figure 2e,f. Cuts approximately 50 μm wide can also heal within 5 min when water is sprayed on the damaged coating. Remarkably,

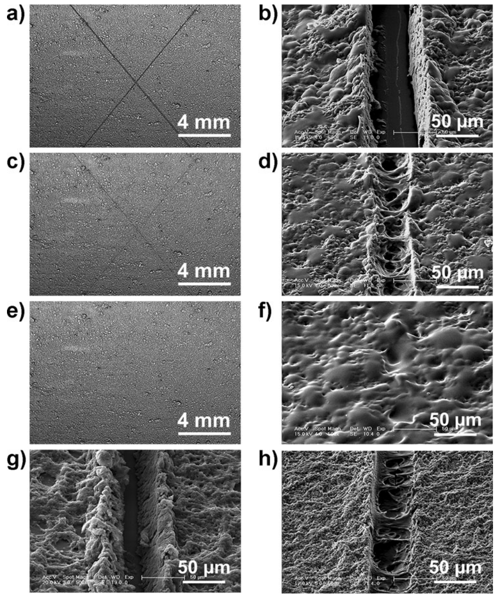

Figure 2. Visual observation of (bPEI10.5/PAA3)*30 and (bPEI6.5/PAA3)*300 coatings with cuts 50 μm wide after different times of immersion in water. a–f) The (bPEI10.5/PAA3)*30 coating immersed in water for 0 s (a,b), 10 s (c,d), and 5 min (e,f). g,h) The (bPEI6.5/PAA3)*300 coating immersed in water for 0 s (g) and 24 h (h).

when the damaged coating in Figure 2a was placed in an environment with a relative humidity of 100% at room temperature, healing of the coating was completed within 1 h. The self-healing abilities of the bPEI10.5/PAA3 coatings are thickness-dependent. To repair a cut roughly 50 μm in width that penetrates to the substrate, the bPEI10.5/PAA3 coating must have at least 25 deposition cycles, which corresponds to a coating thickness of (24.5 ± 2.4) μm (see the Supporting Information). Generally, traditional LbL assembly is time-consuming for fabricating micrometer-thick polyelectrolyte coatings. Exponential LbL assembly overcomes the shortcomings of traditional LbL assembly and provides a rapid way of fabricating coatings with water-enabled self-healing. In a control experiment, a slowly deposited (bPEI6.5/PAA3.0)*300 coating of thickness (29.4 ± 2.9) μm failed to heal cuts approximately 50 μm wide, even when the damaged coating was immersed in water at room temperature for 24 h (Figure 2g,h).

Cyclic voltammetry (CV) was used to further confirm the self-healing of the damaged (bPEI10.5/PAA3)*30 coatings in water. In a conventional three-electrode electrochemical cell, an indium–tin–oxide(ITO)-coated glass substrate with a (bPEI10.5/PAA3)*30 coating served as the working electrode. A mixture of *n*-tetrabutylammonium hexafluorophosphate (TBAPF$_6$) (0.1 mol L^{-1}) and acetonitrile was used as the electrolyte solution. Ferrocene (1×10^{-3} mol L^{-1}) dissolved in TBAPF$_6$/acetonitrile electrolyte solution was used as a probe. As shown in Figure 3, a pair of obvious oxidation–reduction peaks corresponding to the oxidation/reduction of ferrocene is observed in the CV curve of the unmodified ITO substrate. However, no current is detected in the CV curve of the ITO substrate covered with a (bPEI10.5/PAA3)*30 coating (detection limit $\approx 10^{-5}$ A), indicating that the (bPEI10.5/PAA3)*30

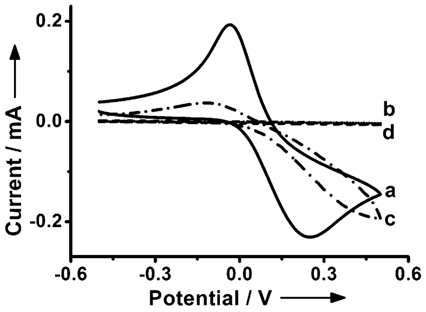

Figure 3. Cyclic voltammograms recorded for ferrocene (1×10^{-3} mol L^{-1}) in acetonitrile (0.1 mol L^{-1} TBAPF$_6$) on ITO electrodes. a) Unmodified ITO electrode, b) ITO electrode deposited with a (bPEI10.5/PAA3)*30 coating, c) ITO electrode in (b) with cuts roughly 50 μm wide made on the coating. d) ITO electrode in (c) after the electrode had been immersed in water for 5 min. The scan rate is 0.05 V s^{-1}. For clarity, the scale on the *y* axis for curves b, c, and d was multiplied by 10.

coating is compact and impermeable to ferrocene. When cuts roughly 50 μm wide were made on the (bPEI10.5/PAA3)*30 coating using a scalpel, currents corresponding to the oxidation/reduction of ferrocene on the ITO substrate were again detected. The currents are low because the cuts occupy only a limited fraction of the total area of the coating on the ITO substrate. No current was detected for the ITO substrate after the damaged (bPEI10.5/PAA3)*30 coating had been immersed in water for 5 min, confirming that a compact coating impermeable to ferrocene is recovered. The electrochemical tests confirm that the damaged (bPEI10.5/PAA3)*30 coating is perfectly healed in water.

The mechanical properties of the (bPEI10.5/PAA3)*30 and (bPEI6.5/PAA3)*300 coatings under dry conditions and equilibrated in water were measured by atomic force microscopy (AFM) indentation to understand the self-healing mechanism of the (bPEI10.5/PAA3)*30 coatings in water.[12] The indentation loading curves of the (bPEI10.5/PAA3)*30 coating under dry conditions (25 % relative humidity, 25 °C) and equilibrated in water are presented in Figure 4, curves a and b. The slope in the contact parts of the indentation loading curve, which is indicative of the stiffness of the coating, decreased significantly when the (bPEI10.5/PAA3)*30 coating was immersed in water, indicating that the coating is significantly softened in water. The (bPEI6.5/PAA3)*300 coating is also softened in water but to a lesser extent, as shown by the fact that the slope of the indentation loading curve in water decreases slightly compared with that under dry conditions (Figure 4, curves c and d). It is notable that under ambient conditions with 25 % relative humidity, a water layer exists on both the coating surface and AFM tip. When the AFM tip approaches the coating surface, capillary forces can cause the AFM tip to jump into contact with the coating, which leads to downward deflections in curves a and c in Figure 4. Based on the indentation loading curves, the Young's moduli of the coatings can be calculated using a classic Hertz model (see the Supporting Information).[13] The (bPEI10.5/PAA3)*30 coatings under dry conditions and in water have Young's moduli of (11.8 ± 2.1) GPa and (0.44 ± 0.10) MPa, respectively. The Young's modulus of the (bPEI10.5/PAA3)*30 coatings in water is more than 26000 times lower than that under dry conditions. In contrast, the Young's moduli of the (bPEI6.5/PAA3)*300 coatings in air and in water are (16.6 ± 4.3) GPa and (0.19 ± 0.06) GPa, respectively. Immersion in water decreases the Young's modulus of the (bPEI6.5/PAA3)*300 coatings by a factor of 87. The LbL-assembled PEM coatings can generally absorb water because they have an ionic cross-linking network structure and polyelectrolytes are hydrophilic in nature.[14] The exponentially growing (bPEI10.5/PAA3)*30 coatings have a higher diffusion of polyelectrolytes and a lower ionic cross-linking density than the slowly deposited (bPEI6.5/PAA3)*300 coatings have. The (bPEI10.5/PAA3)*30 coatings are therefore more easily swollen in water than the (bPEI6.5/PAA3)*300 coatings are. When a dried (bPEI10.5/PAA3)*30 coating with cuts or incisions is immersed in water, the highly swollen and softened coating has a strong tendency to flow to fill in the gaps caused by the damage. The polyelectrolytes on the fractured surfaces come into contact and become intermixed through the electrostatic interaction of freely charged groups in the fractured surfaces. In this way, the damage to the (bPEI10.5/PAA3)*30 coating is repaired. A previous study showed that two substrates coated with PEM films adhere strongly in the presence of water; this demonstrates the strong tendency of polyelectrolytes to interdiffuse at the contacted interface.[15] In contrast, the (bPEI6.5/PAA3)*300 coating, with a higher ionic cross-linking density, is slightly swollen by water, and cannot flow long distances to repair damage.

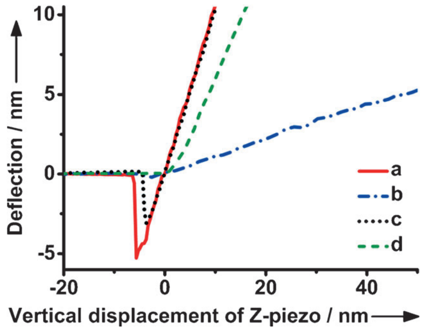

Figure 4. Representative deflection–displacement loading curves of bPEI/PAA coatings under dry conditions and in water. a,b) The (bPEI10.5/PAA3)*30 coating under dry conditions (a) and in water (b). c,d) The (bPEI6.5/PAA3)*300 coating under dry conditions (c) and in water (d).

The self-healing abilities of the exponentially growing bPEI10.5/PAA3 coatings originate from the high flowability of the coatings and the interdiffusion of polyelectrolytes at the fractured surfaces in the presence of water. These properties endow such coatings with the following advantages as intrinsic self-healing materials. 1) Full healing of the damaged coatings can be conveniently accomplished by immersing the coatings in water or spraying water on the coatings. Treatment with water is more easily available than other methods, such as light irradiation or thermal treatment, as a means of healing the damaged coatings. 2) The processes of damaging and healing can be repeated multiple times to heal recurrent damage in the same area. Cuts roughly 50 μm in width are hardly seen after the cutting–healing process has been repeated five times on a (bPEI10.5/PAA3)*30 coating in the same area (see the Supporting Information). 3) The self-healing of the coatings is independent of the waiting time after damage. Cuts on the (bPEI10.5/PAA3)*30 coating were completely healed even when the damaged coating was first stored in an ambient environment with a relative humidity of 20–25 % at room temperature for 7 d and then immersed in water to conduct the self-healing (see the Supporting Information). The bPEI10.5/PAA3 coatings therefore do not need to be repaired immediately after damage appears. This is quite different from the case with self-healing supramolecular rubber derived from ditopic and tritopic molecules associated by hydrogen bonds, whose self-healing ability decreases with waiting time.[5b] The flowability-based healing mechanism means that the healing abilities of the coatings are thickness-dependent because a thicker coating can flow to heal a wider cut. It is worth noting that the high Young's modulus of (11.8 ± 2.1) GPa for (bPEI10.5/PAA3)*30 coatings under ambient conditions implies that the coatings are mechanically stable enough for practical use. The high Young's modulus of the (bPEI10.5/PAA3)*30 coatings benefits from the high molecular weight of the bPEI and PAA building blocks. Most importantly, the concept of exponential LbL assembly of self-healing polyelectrolyte coatings is applicable to the fabrication of other kinds of self-healing coatings. For example, exponential LbL assembly of bPEI ($M_w \approx 25000$, 4 mg mL^{-1}, pH 10.5) and hyaluronic acid (HA) ($M_w \approx 800000$, 4 mg mL^{-1}, pH 3) led to the successful fabrication of self-healing bPEI10.5/HA3 coatings with smooth surfaces.[16] The (bPEI10.5/HA3)*50 coatings have an average thickness of (36.6 ± 1.4) μm. AFM indentation measurements reveal that the (bPEI10.5/HA3)*50 coatings under dry conditions and equilibrated in water have Young's moduli of (10.5 ± 2.5) GPa and (17.7 ± 5.3) kPa, respectively. The (bPEI10.5/HA3)*50 coatings can heal cuts roughly 50 μm wide within 5 min when immersed in water, with a self-healing behavior similar to that of (bPEI10.5/PAA3)*30 coatings (see the Supporting Information).

In summary, we have demonstrated that intrinsic self-healing polyelectrolyte coatings can be rapidly fabricated by exponentially growing LbL-assembled polyelectrolyte multilayers. The repair of cuts with widths and depths of several tens of micrometers on these coatings can be conveniently accomplished by immersing the coatings in water or spraying water on the coatings. Moreover, the self-healing of the polyelectrolyte coatings, which is independent of the waiting time after damage, can be repeated multiple times in the same area. We clarified that LbL-assembled polyelectrolyte coatings of high flowability in water are important for achieving the water-enabled self-healing function. The self-healing mechanism revealed in this study can be used in the design of various kinds of self-healing polyelectrolyte coatings, and these are expected to be useful in the production of protecting layers, biomaterials coatings, and display devices.

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[1] a) S. D. Bergman, F. Wudl, *J. Mater. Chem.* **2008**, *18*, 41–62; b) R. P. Wool, *Soft Matter* **2008**, *4*, 400–418; c) J.-L. Wietor, R. P. Sijbesma, *Angew. Chem.* **2008**, *120*, 8282–8284; *Angew. Chem. Int. Ed.* **2008**, *47*, 8161–8163; d) M. D. Hager, P. Greil, C. Leyens, S. van der Zwaag, U. S. Schubert, *Adv. Mater.* **2010**, *22*, 5424–5430; e) B. J. Blaiszik, S. L. B. Kramer, S. C. Olugebefola, J. S. Moore, N. R. Sottos, S. R. White, *Annu. Rev. Mater. Res.* **2010**, *40*, 179–211; f) M. M. Caruso, D. A. Davis, Q. Shen, S. A. Odom, N. R. Sottos, S. R. White, J. S. Moore, *Chem. Rev.* **2009**, *109*, 5755–5798.

[2] a) D. G. Shchukin, H. Möhwald, *Small* **2007**, *3*, 926–943; b) J.-H. Park, P. V. Braun, *Adv. Mater.* **2010**, *22*, 496–499; c) S. H. Cho, S. R. White, P. V. Braun, *Adv. Mater.* **2009**, *21*, 645–649.

[3] a) A. P. Esser-Kahn, N. R. Sottos, S. R. White, J. S. Moore, *J. Am. Chem. Soc.* **2010**, *132*, 10266–10268; b) S. R. White, N. R. Sottos, P. H. Geubelle, J. S. Moore, M. R. Kessler, S. R. Sriram, E. N. Brown, S. Viswanathan, *Nature* **2001**, *409*, 794–798.

[4] a) K. S. Toohey, N. R. Sottos, J. A. Lewis, J. S. Moore, S. R. White, *Nat. Mater.* **2007**, *6*, 581–585; b) C. J. Hansen, W. Wu, K. S. Toohey, N. R. Sottos, S. R. White, J. A. Lewis, *Adv. Mater.* **2009**, *21*, 4143–4147.

[5] a) X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran, F. Wudl, *Science* **2002**, *295*, 1698–1702; b) P. Cordier, F. Tournilhac, C. Soulié-Ziakovic, L. Leibler, *Nature* **2008**, *451*, 977–980; c) M. Burnworth, L. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan, C. Weder, *Nature* **2011**, *472*, 334–338; d) G. Deng, C. Tang, F. Li, H. Jiang, Y. Chen, *Macromolecules* **2010**, *43*, 1191–1194; e) A. S. J. Iyer, L. A. Lyon, *Angew. Chem.* **2009**, *121*, 4632–4636; *Angew. Chem. Int. Ed.* **2009**, *48*, 4562–4566.

[6] a) G. Decher, *Science* **1997**, *277*, 1232–1237; b) F. Caruso, R. A. Caruso, H. Möhwald, *Science* **1998**, *282*, 1111–1114; c) X. Zhang, H. Chen, H. Zhang, *Chem. Commun.* **2007**, 1395–1405.

[7] a) D. G. Shchukin, M. Zheludkevich, K. Yasakau, S. Lamaka, M. G. S. Ferreira, H. Möhwald, *Adv. Mater.* **2006**, *18*, 1672–1678; b) Y. Li, L. Li, J. Sun, *Angew. Chem.* **2010**, *122*, 6265–6269; *Angew. Chem. Int. Ed.* **2010**, *49*, 6129–6133.

[8] Y. Lu, X. Chen, W. Hu, N. Lu, J. Sun, J. Shen, *Langmuir* **2007**, *23*, 3254–3259.

[9] A. B. South, L. A. Lyon, *Angew. Chem.* **2010**, *122*, 779–783; *Angew. Chem. Int. Ed.* **2010**, *49*, 767–771.

[10] a) C. Picart, P. Lavalle, P. Hubert, F. J. G. Cuisinier, G. Decher, P. Schaaf, J.-C. Voegel, *Langmuir* **2001**, *17*, 7414–7424; b) C. Picart, J. Mutterer, L. Richert, Y. Luo, G. D. Prestwich, P. Schaaf, J.-C. Voegel, P. Lavalle, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 12531–12535.

[11] a) P. Podsiadlo, M. Michel, J. Lee, E. Verploegen, N. W. S. Kam, V. Ball, J. Lee, Y. Qi, A. J. Hart, P. T. Hammond, N. A. Kotov, *Nano Lett.* **2008**, *8*, 1762–1770; b) B. Sun, C. M. Jewell, N. J. Fredin and D. M. Lynn, *Langmuir* **2007**, *23*, 8452–8459; c) J. Fu, J. Ji, L. Shen, A. Küller, A. Rosenhahn, J. Shen, M. Grunze, *Langmuir* **2009**, *25*, 672–675.

[12] a) X. Wang, Z. Niu, S. Li, Q. Wang, X. Li, *J. Biomed. Mater. Res. Part A* **2008**, *87*, 8–14; b) A. Reisch, M. D. Moussallem, J. B. Schlenoff, *Langmuir* **2011**, *27*, 9418–9424.

[13] M. Radmacher, M. Fritz, C. M. Kacher, J. P. Cleveland, P. K. Hansma, *Biophys. J.* **1996**, *70*, 556–567.

[14] Y. Ma, Y. Zhang, B. Wu, W. Sun, Z. Li, J. Sun, *Angew. Chem.* **2011**, *123*, 6378–6381; *Angew. Chem. Int. Ed.* **2011**, *50*, 6254–6257.

[15] D. Matsukuma, T. Aoyagi, T. Serizawa, *Langmuir* **2009**, *25*, 9824–9830.

[16] The (bPEI10.5/HA3)*n coatings were fabricated in a similar way to that used for (bPEI/PAA)*n coatings by replacing the aqueous PAA solution with aqueous HA (pH 3.0) solution.

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