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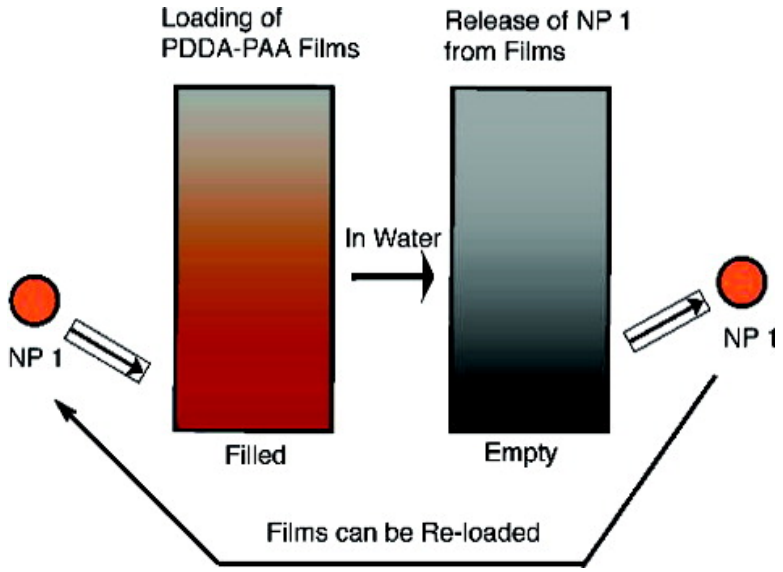
J. Am. Chem. Soc., **2008**, 130 (12), 3748-3749 • DOI: 10.1021/ja7110288



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Published on Web 03/06/2008

Reversible Loading and Unloading of Nanoparticles in "Exponentially" Growing Polyelectrolyte LBL Films

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The layer-by-layer (LBL) assembly, based on sequential adsorption of oppositely charged components, is one of the most established methods for the preparation of thin films with controlled properties.[1,2] The LBL technique is not limited to polyelectrolytes, but almost any type of macromolecular species (charged preferred) including inorganic molecular clusters,[3] nanoparticles (NPs),[4−5] nanowires,[6] organic dyes,[7] polypeptides,[8] DNA,[9] or viruses[10] can be used as the assembly components. Most of these LBL films have been loaded with active molecules *only during the preparation* by using the species of interest as active constituents in the film buildup. The significance of finding a method to reversibly load and unload NPs in LBL films is 4-fold. (1) Most obviously, it would enable fast and universal preparation of NP-based coatings with a variety of functionalities. (2) The mobility of NPs inside the polymeric matrix would enable new methods of control over self-assembly processes.[11] (3) A dynamic exchange process is essential in the development of fine separation tools for NPs. (4) Last but not the least, it would create important opportunities for biomedical applications using organic/inorganic nanocolloids, proteins, DNA, RNA, etc. in controlled-release devices.

Recent advances in the fundamental studies of LBL films suggest that the highly hydrated exponentially growing films[12] can incorporate multivalent ions,[13] dyes,[14] and small drugs.[15] These compounds can be released upon triggering by an external signal, e.g., an ion exchange process,[13a] or a change in the pH.[14] Along the same lines, it was also observed that some LBL films are deformed when put in contact with colloidal particles.[16] Using these findings as a foundation one can hypothesize that LBL films can indeed have the ability to load/unload nanoscale species in a controlled fashion. The concept of loading and unloading an LBL film after its buildup would be of real interest and has not been validated very well yet. It has just been observed that certain combinations of polyelectrolytes allow for the completely irreversible loading of proteins or nanoparticles.[17] The fundamental possibility of reversible loading−unloading processes is the subject of this communication and is essential for enabling applications mentioned above.

To demonstrate this functionality we used exponentially growing LBL films made from poly(diallyldimethylammonium chloride) (PDDA) and poly(acrylic acid) (PAA). The films were prepared by dipping alternatively a glass substrate in 0.5% w/v PDDA and 1% w/v PAA solutions. We note that exponential growth in the PDDA/PAA system is quite unusual and to our knowledge has not been reported yet (see Supporting Information). Exponential growth stipulates an increased mobility of the polymer chains in the films,[12] which, in turn, opens the possibility for fairly large colloids to penetrate inside them. In the initial experiments we used negatively charged thioglycolic acid-capped CdTe quantum dots (NP**1**, Figure 1a, 4 nm diameter, zeta potential = −50 mV). As prepared (PDDA/PAA)$_n$ films, with $n = 45$ (where n is the number of LBL deposition cycles), were exposed to a CdTe suspension at pH 9 (Figure 1a). After 7 h of exposure, the films appeared highly swollen and displayed characteristic adsorption and luminescence of NPs (Figure 1a, inset). Release of the incorporated CdTe and reproducibility were demonstrated by immersing the CdTe-loaded films in pure water at pH 9. The swollen films turned colorless in ∼30 h indicating release of NP**1** from the films (Figure 1a).

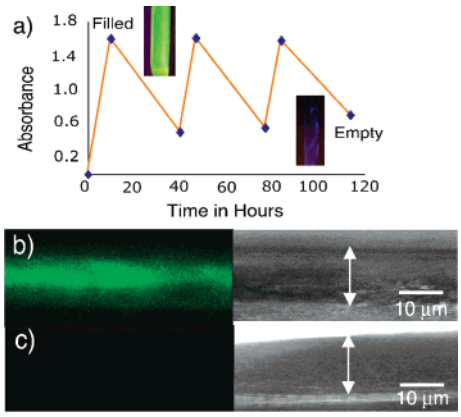

Figure 1. (a) Loading and unloading of (PDDA-PAA)$_{45}$ films (pH 9) with green fluorescence-emitting NP**1** as followed by UV−vis absorbance at 530 nm (note the large change in absorbance). The insets are fluorescence photographs of the filled (top) and empty (bottom) films. (b) Confocal microscopy images of (PDDA-PAA)$_{100}$ films loaded by 6 h of exposure to NP1 solution and (c) empty films after 24 h exposure to pH 9 water. The right panels show white light images.

Clear evidence of loading and unloading of NP**1** in (PDDA-PAA)$_{100}$ multilayer films was obtained by confocal microscopy of the cross sections (Figure 1b). After loading for 6 h, the films appeared to be evenly filled with the NPs. The fluorescence signal disappeared after the loaded films were placed in contact with pH 9 water for 24 h (Figure 1c) under identical conditions. Bright field optical images of cross sections show no microscale morphological changes of the films between the two loaded and empty states (Figure 1b,c, right panels). Distribution of NPs in the film may not necessarily be uniform and can involve both lateral and vertical gradients.

To better understand the loading/unloading mechanism, we measured the release kinetics of NP**1** in water at pH 9 and 7 and in films covered with a capping layer of a linear polyelectrolytes LBL combination of (PDDA-PSS)$_{10}$.[18] In the past, it was demonstrated that exponentially growing LBL films can be capped with impermeable capping layers made either from linearly growing LBL films[18] or from hydrolyzable polyesters.[19] We found that the pH 9 environment resulted in the release of the NPs in a characteristic

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10.1021/ja7110288 CCC: $40.75

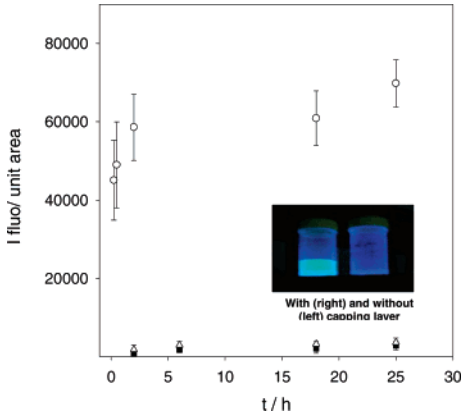

Figure 2. Release of NP**1** from $(PDDA\text{-}PAA)_{100}$ as measured by fluorescence intensity of the solution in contact with pure water at pH 9 (○) and 7 (■). Effect of capping of the film by a $(PDDA\text{-}PSS)_{10}$ film (△) after particle loading in presence of water at pH 9. Six experiments/point, error bars correspond to ± 1 standard error. The inset shows the fluorescence of the supernatant at pH 9 (left) and of the $(PDDA\text{-}PSS)_{10}$ capped film (right).

time of ~3−10 h. At pH 7, the amount of released particles was at least 2 orders of magnitude lower than that at pH 9 even after 25 h (Figure 2). The reason for this difference is that the fraction of negatively charged carboxylate groups at pH 7 is lower than that at pH 9, hence creating a larger excess of positively charged groups in the film (protonation of the quaternary ammonium groups of PDDA is pH independent) and resulting in increasing the interactions between NP**1** and the LBL film. However, when the NP**1** loaded $(PDDA\text{-}PAA)_{100}$ film was capped with a linear LBL film of $(PDDA\text{-}PSS)_{10}$, the NPs got trapped inside the films. The release kinetics of NP**1** was found comparable to that found at pH 7 (Figure 2). This trend was also confirmed by the fluorescence of the solutions used to extract the NP**1** for 25 h (inset in Figure 2).

The fluorescence intensity of the NP**1** suspension before and after the loading of $(PDDA\text{-}PAA)_{100}$ films was used for estimating the concentration of NP**1** incorporated in the films, and it was found to be 300 ± 50 mg/mL. This corresponds to a volume fraction of ~30%, which is quite high. The corresponding partition coefficient in the film with respect to the solution is 60 ± 10 (see Supporting Information). The fact that the loading−unloading of the film is reversible allows using Boltzman's statistics to evaluate the stabilization energy of the NP**1** in the film. It can be calculated to be 4 k_BT, which is significant but should not impede the release kinetics of the NPs, as is indeed observed. When the film is topped with a positively charged PDDA layer, the partition coefficient increases to 80 ± 15. In order to estimate the amount of NPs released after 30 h into pH 9 water, the fluorescence of the solution in contact with the film was regularly measured. Upon integrating the fluorescence due to the release of NP**1**, it appeared that at least 60−70% of the NPs incorporated in the films were released, which can also be seen in Figure 1a.

The fact that not all of the fluorescence is recovered, which was expected in the case of quantitative release, can be due to partial trapping of the NPs in the films or to quenching of the fluorescence in the supernatant due to the aggregation of particles. Figure 1c shows that the release is close to quantitative hence the assumption of particle aggregation leading to fluorescence quenching has to be made. The mass fraction of NP**1** inside the $(PDDA\text{-}PAA)_{100}$ film was also obtained by thermogravimetric analysis (TGA). Compared to $(PDDA\text{-}PAA)_{100}$ alone, there was a residual mass corresponding to 20−22% of the initial mass of the film when loaded with NP**1.** This result is consistent with the volume fraction obtained by the depletion experiments.

One technological prospect for opening by reversible loading and unloading mentioned above is NP separation. To demonstrate this and to ascertain the mechanism of the NP**1** association in the film, we synthesized positively charged NP**2** using 2-(dimethylamino)ethanethiol (DMAET) as a stabilizer (zeta potential = +1.2 mV). Depletion measurements indicate that they display a partition coefficient of (10 ± 3). This result was also confirmed by TGA (7−8% of the film mass remains). This is indeed significantly lower than that for the negatively charged NP**1** but overall remains fairly high, which points to incorporation of negatively charged NPs due to extrinsic charge compensation in the films similar to that found in ion exchange membranes[12] and nonelectrostatic interactions between NPs and polymers.[20] These observations indicate preferential selectivity of incorporation and release of NPs in such films.

In summary, we demonstrate here for the first time postassembly reversible loading and unloading of NPs in a swollen polyelectrolyte film. The variations of the structure of the LBL layers (capping/topping layer) and the NPs can be used to control the incorporation and release of the NPs, making possible sophisticated sensing, protective, biological, and optoelectronic functionalities.

Acknowledgment. The work is supported by AFOSR MURI 444286-P061716, ONR N00014-06-1-0473, Air Force FA9550-05-1-043, NSF CMS-0528867, and NSF R8112-G1. P.P. thanks the Fannie and John Hertz Foundation for support of his work through a graduate fellowship. V.B. acknowledges the "Commission Franco-Américaine", the Fulbright Foundation, and Région Alsace for Financial support.

Supporting Information Available: Description of film buildup, NP synthesis, and characterization. $(PDDA\text{-}PAA)_n$ film thickness as a function of the number of layers. TGA curves and pictures showing the film swelling upon loading with NP**1**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Decher, G. *Science* **1997**, *277*, 1232.
(2) Ariga, K.; Hill, J. P.; Ji, Q. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2319.
(3) Keller, S. W.; Kim, H. N.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 8817.
(4) Kotov, N. A.; Dekany, I.; Fendler, J. H. *J. Phys. Chem.* **1995**, *99*, 13065.
(5) Caruso, F.; Lichtenfeld, H.; Giersig, M.; Möhwald, H. *J. Am. Chem. Soc.* **1998**, 120, 8523.
(6) (a) Tang, Z. Y.; Kotov, N. A.; Giersig, M. *Science* **2002**, *297*, 237. (b) Gunawidjaja, R.; Jiang, C.; Peleshanko, S.; Ornatska, M.; Singamaneni, S.; Tsukruk, V. V. *Adv. Funct. Mater.* **2006**, *16*, 2024.
(7) Nicol, E.; Habib-Jiwan, J. L.; Jonas, A. M. *Langmuir* **2003**, *19*, 6178.
(8) Lvov, Y.; Ariga, K.; Ichinose, I.; Kunitake, T. *J. Am. Chem. Soc.* **1995**, *117*, 6117.
(9) Lvov, Y.; Decher, G.; Sukhorukov, G. B. *Macromolecules* **1993**, *26*, 5396.
(10) Dimitrova, M.; Arntz, Y.; Lavalle, Ph.; Meyer, F.; Wolf, M.; Schuster, C.; Haïkel, Y.; Voegel, J.-C.; Ogier, J. *Adv. Funct. Mater.* **2007**, *17*, 233.
(11) (a) Tang, Z. Y; Kotov, N. A.; Giersig, M. *Science* **2002**, *297*, 237. (b) Tang, Z. Y.; Zhang, Z. L.; Wang, Y.; Glotzer, S. C.; Kotov, N. A. *Science* **2006**, *314*, 274. (c) Tang, Z. Y.; Wang, Y.; Shanbhag, S.; Giersig, M.; Kotov, N. A. *J. Am. Chem. Soc.* **2006**, *128*, 6730.
(12) Picart, C.; Lavalle, Ph.; Hubert, P.; Cuisinier, F. J. G.; Decher, G.; Schaaf, P.; Voegel, J. C. *Langmuir* **2001**, *17*, 7414.
(13) (a) Hübsch, E.; Fleith, G.; Fatisson, J.; Labbé, P.; Voegel, J.-C.; Schaaf, P.; Ball, V. *Langmuir*, **2005**, 21, 3664. (b) Takita, R.; Yoshida, K.; Anzai, J. *Sens.Actuators, B* **2007**, *121*, 54.
(14) Burke, S. E.; Barrett, C. J. *Macromolecules* **2004**, *37*, 5375.
(15) Vodouhê, C.; Le Guen, E.; Mendez, Garza, J.; Francius, G.; Déjugnat, C.; Ogier, J.; Schaaf, P.; Voegel, J.-C.; Lavalle, Ph. *Biomaterials* **2006**, *27*, 4149.
(16) (a) Picart, C.; Sengupta, K.; Schilling, J.; Maurstad, G.; Ladam, G.; Bausch, A. R.; Sackmann, E. *J. Phys. Chem. B* **2004**, *108*, 7196. (b) Volodkin, D.; Arntz, Y.; Schaaf, P.; Möhwald, H.; Voegel, J.-C.; Ball, V. *Soft Matter* **2008**, *4*, 122.
(17) (a) Schlenoff, J. B.; Salloum, D. S. *Biomacromolecules* **2004**, *5*, 1089. (b) Wang, L.; Wang, X.; Xu, M.; Chen, D.; Sun, J. *Langmuir* **2008**, *24*, 1902.
(18) Mendez Garza, J.; Schaaf, P.; Muller, S.; Ball, V.; Stoltz, J.-F.; Voegel, J.-C.; Lavalle, Ph. *Langmuir* **2004**, *20*, 7298.
(19) Mendez Garza, J.; Jessel, N.; Ladam, G.; Dupray, V.; Muller, S.; Stoltz, J.-F.; Schaaf, P.; Voegel, J.-C.; Lavalle, Ph. *Langmuir* **2005**, *21*, 12372.
(20) Farhat, T. R.; Schlenoff, J. B. *J. Am. Chem. Soc.* **2003**, *125*, 4627.

JA7110288