Controlled Interfacial Permeation, Nanostructure Formation, Catalytic Efficiency, Signal Enhancement Capability, and Cell Spreading by Adjusting Photochemical Cross-Linking Degrees of Layer-by-Layer Films

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ABSTRACT: Interfacial properties including permeation, catalytic efficiency, Raman signal enhancement capabilities, and cell spreading efficiencies are important features that determine material functionality and applications. Here, we propose a facile method to adjust the above-mentioned properties by controlling the cross-linking degrees of multilayer using a photoactive molecule. After treating the cross-linked films in basic solutions, films with different cross-linking degrees presented varying residue thicknesses and film morphologies. As a result, these different films possessed distinct molecular loading and release characteristics. In addition, gold nanoparticles (AuNPs) of different morphological traits were generated by redox reactions coupled with diffusion within these films. The AuNP–polyelectrolyte obtained from the polyelectrolyte films of the medium cross-linking degrees displayed the highest catalytic efficiency and signal enhancement capabilities. Furthermore, cells responded to the variation of film cross-linking degrees, and on the films with the highest cross-linking degree, cells adhered with the highest speed. We expect this report to provide a general interfacial material engineering strategy for material designs.

KEYWORDS: layer-by-layer, photochemical cross-linking, interfacial permeation, catalytic efficiency, signal enhancement capability, cell spreading

1. INTRODUCTION

The layer-by-layer (LbL) technique is a general strategy for engineering the interfacial properties of materials due to its versatility, which stems from its simplicity and tunability.1,2 In order to handle the stability problem of the multilayers under extreme conditions (e.g., in solutions with high ionic strengths), researchers have proposed the use of covalently cross-linked LbL multilayers.3–8 These LbL multilayers normally enhance film stability through transfer of the interlayer weak interactions within the film to covalent bonds. Because of the enhanced film stabilities, covalently cross-linked films have led to various new functions and applications, such as patterned surfaces,9 molecularly imprinted films,10 anticorrosion or protective films,11 stable and flexible substrates for arrays that were produced by multistep chemical reactions,12 and durable films to selectively absorb ions.13 Furthermore, as a result of cross-linking, the increased rigidity of the LbL films has also been employed to study cell responses and the LbL multilayers are proved to be promising biomaterials.14–16 While most of the above-mentioned studies employed covalently held films with the highest possible cross-linking degree, very little research has been conducted with regard to the influence of the cross-linking degrees on the material performance of multilayers.17 These previous studies concerning the adjustment of cross-linkage degree have, however, demonstrated that film permeation and film rigidity could be altered by variation of cross-linking degrees. Consequently, adjustable interfacial functionalities including delayed release and cell adhesion as well as spreading were realized using LbL films by varying film cross-linking degrees.

In general, interfacial functionalities are crucial to material performance. Besides permeation and rigidity, other material

Received: August 19, 2016
Accepted: September 26, 2016
Published: September 26, 2016

DOI: 10.1021/acsami.6b10453
ACS Appl. Mater. Interfaces 2016, 8, 34080–34088
properties such as reactivity or signal enhancement capability that stem from nanoscopic structures also hold a high importance in various applications. In this study, we tuned the cross-linking degrees of LbL films and subsequently were able to adjust a variety of important interfacial properties. We first prepared the covalently cross-linked film using a photochemical strategy developed by our group, which we termed "post infiltration followed by photochemical cross-linking." This method has provided wide applications in interfacial assembly of functional nanostructures.18 Using this method, we once prepared the PAH/PAA films using the conventional LbL assembly method, a bifunctional photoactive small molecule 4,4′-diazido-2,2′-stilbenedisulfonic acid disodium (DAS) with azido groups was infiltrated into the multilayers, and then, photochemical reaction was employed to cross-link the films. In this study, we proceeded to fine-tune film cross-linking degrees by adjusting the infiltration period of the photoactive molecule. This study revealed that increased cross-linking degrees can enhance film stability in a hostile environment to varying extents and resulted in films with varying morphologies, permeation, molecular loading capacities, and release profiles of the incorporated molecules (Scheme 1). Subsequently, gold nanoparticles (AuNPs) with different morphologies, and thus varying catalytic performance and signal enhancement efficiencies, were generated in these films using redox reactions coupled with diffusion by controlling the film cross-linking degrees. Interestingly, the polyelectrolyte–AuNP composite interfaces that were produced from films with the medium cross-linking degree showed the highest catalytic and signal enhancement performance. In addition, the cross-linking degrees also dictated different cell behaviors on top of these films. We expect these findings to significantly widen application potentials of the LbL technique, allowing researchers to produce multifunctional interfaces in a variety of fields including biomedical materials and energy materials.

2. EXPERIMENTAL SECTION

2.1. Materials and Instruments. The following chemicals were used as supplied and obtained from Sinopharm Chemical Reagent (Beijing Co., Ltd.). H2O2 (30 wt %), NaOH, HAuCl4·3H2O, NH4H2(80%), and H2SO4. Poly(allylamine hydrochloride) (PAH) (Mn = 15 000), poly(acrylic acid) (PAA) (Mn = 240 000), 4-nitrophenol, tetraakis (4-carboxyphenyl) porphyrin (Por), and fluorescein disodium salt were purchased from Sigma-Aldrich. 4,4′-Diazido-2,2′-stilbenedisulfonic acid disodium (DAS) was purchased from TCI. 400 visible spectra were obtained on a Hitachi U-3900H spectrophotometer. Photochemical cross-linking was conducted by employing a commercially available multiwavelength 400 W high-pressure mercury lamp with the light wavelength range of 300–400 nm. The surface morphology of the polyelectrolyte multilayers was characterized with an atomic force microscopy (AFM, Dimension 3100) from Veeco, U.S.A. The cyclic voltammetry scanning (CV) was carried out on a CHI660e electrochemical workstation (Chenhua, Shanghai, China). The thickness of multilayers was measured with a spectroscopic ellipsometer M-2000, U.S.A. A scanning electron microscope (SEM, JSM 7401) was used to characterize the morphology of multilayers embedded with gold nanoparticles. The Raman spectroscopy was measured by a Micro-Raman spectrometer (Horiba).

2.2. Assembly of PAH/PAA Multilayers. The substrate (quartz substrate or silica wafer) was treated with a piranha solution (H2SO4/H2O2 = 7:3 v/v) and washed with copious amounts of water. (CAUTION: "Piranha solution reacts violently with organic materials; it must be handled with extreme care.) The LbL assembly process of PAH/PAA multilayers was carried out as previously reported.9,10 First, the quartz substrate was immersed in PAH solution (1 mg·mL−1, pH 9.4) for 20 min, washed with water, and dried under a nitrogen flow. Second, the quartz substrate was transferred to a PAA solution (1 mg·mL−1, pH 4.8) for 20 min, washed with pure water, and dried under a nitrogen flow. Third, the above two steps were alternatively deposited in cycles until the desired number of bilayers were obtained. In the CV experiments, multilayers were prepared on the gold electrode surface instead of on quartz substrate.

2.3. Photochemical Cross-Linking of the Multilayers with Varying Cross-Linking Degrees and Subsequent Treatment in Basic Solutions. The substrate with (PAH/PAA)6.5 (the subscripts denote the number of PAH/PAA layer and half for PAH) multilayers was immersed into an aqueous solution of DAS (5 mg·mL−1) for 10 s, 3 min, and 30 min, followed by photochemical cross-linking to obtain the multilayers with low, medium, and high cross-linking degrees. The photochemical cross-linking was carried out by irradiation with a 400 W high-pressure mercury lamp from a distance of 20 cm with an intensity of 2.5 mW·cm−2 for 120 s without any filters. Following the photochemical cross-linkages, the substrates were immersed into aqueous solutions of NaOH (pH 11.5) for 10 min, unless otherwise noted.

2.4. Loading and Release of Fluorescein Sodium from the Multilayered Film. The film for fluorescein sodium loading and
release was prepared in a process similar to the process described in Section 2.2. After the assembly, cross-linking, and basic treatment process, the substrate was immersed in a fluorescein sodium solution (0.2 mg·mL$^{-1}$) for 4 h to load fluorescein sodium. The release of fluorescein sodium was carried out in PBS (pH 7.4, 9 mL) by immersing the substrate in the solution. Five sets of parallel experiments were carried out.

2.5. Formation of AuNPs on Multilayered Films and Assembly of the Catalytic Device. The multilayered films of varying cross-linking degrees were first treated in basic solutions (adjusted by NaOH, pH 11.5) for 3 min. Then, the films were immersed in a solution of hydrazine hydrate (8 wt %) for 3 min. The film with the medium cross-linking degrees absorbed the largest amount of N$_2$H$_4$ according to pH test results (After being immersed in N$_2$H$_4$ solution, the film was placed into 10 mL of PBS to release the N$_2$H$_4$ for 120 min, and the pH values of the solution after release was 8.06 for the film with the low cross-linking degree, 8.15 for the medium cross-linking degree, and 7.74 for the high cross-linking degree.) The amount of absorbed N$_2$H$_4$ was thus calculated as 2.7 × 10$^{-4}$ mol for the low cross-linked film, 3.8 × 10$^{-4}$ for the medium cross-linked, and 8.9 × 10$^{-5}$ for the high cross-linked film. Immediately after being lifted up from the hydrazine hydrate solution, the substrates were then immersed into an aqueous solution of 20 mmol·L$^{-1}$ chloroauric acid for 3 min. AuNPs were generated in the films during this final immersion.

The fluidic catalytic device was assembled using two pieces of surface-engineered quartz substrate with the lateral size of 1 × 3 cm, spaced, and sealed by a piece of PDMS with a thickness of 2 mm that held open space in the center area, schematically shown in Figure 5e. The solution of 4-NP was held open space in the center area, schematically shown in Figure 5e. After DAS loading, UV irradiation was applied to cross-link these films. Upon UV irradiation, DAS decomposes into nitrene radicals and forms covalent bonds with adjacent C–H, N–H, and O–H functional groups.$^{23–25}$ After UV irradiation, the characteristic absorbance of DAS around 340 nm decreased, and absorbance in the adjacent areas at approximately 210–300 and 400 nm increased (Figure 1c). The change in the UV–vis absorbance band indicated that DAS was decomposed to nitrene species and subsequently should form covalent bonds with adjacent reactive functional groups. Following the cross-linking of the multilayers, their stability upon immersion in basic NaOH solutions was studied. The basic environment deionized PAH, broke the electrostatic interactions between PAA and PAH, and thus completely decomposed the uncross-linked multilayers as demonstrated in previous studies.$^{9,25,26}$ In this study, we show that all the cross-linked multilayers were preserved to varying extents after immersion in basic solutions (Figure 1d). After immersion in basic solutions, the film absorbance was lower for all the films. The partial loss of absorbance was attributed to the loss of unreacted DAS and also to a fraction of polyelectrolyte building blocks. The films with low, medium, and high cross-linking degrees displayed low, medium, and high absorbance, respectively.

3. RESULTS AND DISCUSSION

3.1. Film Preparation and Treatment in Basic Solutions. The multilayered films were prepared using the method of "post infiltration followed by photochemical cross-linking".$^9$ Briefly, multilayered (PAH/PAA)$_{6.5}$ were first constructed using the conventional LBL technique: the absorbance of the multilayers increased with the number of bilayers (Figure 1a). The absorbance of the film increased slowly during the first 4 assembly cycles and grew rapidly during assembly cycles 5 and 6. Afterward, the bifunctional photoactive small molecule DAS was infiltrated into the multilayers to serve as a photochemical active cross-linker. DAS gradually accumulated in the multilayers with the prolonged infiltration time of 120 min, as indicated by the gradual growth of its characteristic absorbance at 340 nm (Figure 1b). To control the DAS loading amount in the multilayers, we chose the immersion times of 10 s, 3 min, and 30 min. At the infiltration time of 30 min, the fast adsorption process was complete. The DAS loading densities in these films were 0.2873/0.4692/0.7138 μg·cm$^{-2}$/layer, respectively, calculated from absorbance standard curves of DAS.$^{22}$ These amounts corresponded to 44.4% (10 s infiltration), 62.4% (3 min infiltration), and 87.7% (30 min infiltration) of the largest DAS infiltration amount in these films (80 min infiltration). Correspondingly, the cross-linked films generated were termed "film with low/medium/high" cross-linking degrees.

![Figure 1](image-url)
linking degree was 52 nm, which was 54% of the thickness before rinsing, and the film with the low cross-linking degree was 21 nm thick, only 25% of the thickness before rinsing. The decreased thickness was believed to result from the loss of the building unit, the polyelectrolyte molecules, during the rinsing process and subsequent reorganization of the multilayers. The dramatic difference in thickness after rinsing indicates that the cross-linking degrees play important roles in adjusting the stabilities of the films in a corrosive environment. A confirmation of similar results was found by using ellipsometry (see Table 1).

Consistent with the change in the thicknesses of the multilayers, the morphologies of the films with different cross-linking degrees after rinsing were also obviously different (Figure 2). Before rinsing in basic solutions, all the films presented smooth surfaces without characteristic traits. After rinsing, the film with the low cross-linking degree displayed domains of the largest sizes of around 5 μm. The film with the medium cross-linking degree displayed densely arranged domains of around 500 nm, and the films with the high cross-linking degree presented patterns with the lease domain sizes of around 100 nm.

The generation of the surface morphologies after the rinsing treatment was explained as being the result of the release of strains inside the multilayers after reorganization upon rinsing in the basic solutions. With the loss of the building electrolytes in the multilayers during the rinsing process, the multilayers became less evenly distributed and strains were thus raised because of the in-plane inhomogeneity. The film with the low cross-linking degree lost the most amount of polymeric building blocks during the basic washing and drying process and thus accumulated the largest amount of strain within the film. In order to release the strains, the multilayered films experienced reorganization. In the films with the high cross-linking degree, the building electrolytes were relatively tightly bound by the covalent bonds around them in the direction perpendicular with respect to the substrates and only small-scale in-plane dislocations could take place, resulting in local cracks and small domains in the film. In the film with the low cross-linking degree, the substantial weight loss during the rinsing process dictated relatively large local strains during drying, but the sparse covalent links around a polyelectrolyte chain allowed larger in-plain dislocation of the chain, permitting fewer cracks during drying. As a result, the film with the low cross-linking density, relatively large domains formed. For similar reasons (the interplay between local strain and in-plane freedom), the film with medium cross-linking degree displayed medium domain sizes.

### 3.3. Permeation of Cross-Linked and Treated Films
The film morphological characteristics indicated that the films with different cross-linking degrees lost varying amounts of building blocks and generated in-film open spaces during the basic rinsing process. Thus, we wondered whether these films would display different permeation in the hydrated states. To verify this postulation, an electrochemistry method was employed to measure the permeation of the films, as shown in Figure 3. The films for electrochemical experiments were prepared on the surface of gold electrodes. After rinsing in basic solutions, the films were washed with deionized water and rinsed in electrolyte solutions. K₃Fe(CN)₆ was used as the electrochemically active probing molecules. After basic treatment, the films displayed an interesting performance in the electrochemical experiments. The electrode covered by the film with the low cross-linking degree displayed the largest redox current, the one covered by the film with the high cross-linking degree displayed the lowest redox current, and the one covered...
by the film with the medium degree displayed medium redox current. Both the electrodes covered by the film with the low and the medium cross-linking degrees presented redox peak currents larger than the control electrodes, which was an electrode covered by uncross-linked PAH/PAA multilayers as prepared (without treatment in basic solutions). The electrode covered by the film with the high cross-linking degree presented a redox peak current lower than the control electrode.

These experimental results demonstrated that, for the films with the low and the medium cross-linking degrees, rinsing in basic solutions generated open spaces within the films and promoted the adsorption and diffusion of \( \text{K}_3\text{Fe} (\text{CN})_6 \) within the films. For the film with the high cross-linking degrees, rinsing in basic solution did not generate open spaces in the films effectively, and the covalent bonds served as barriers for the diffusion of \( \text{K}_3\text{Fe} (\text{CN})_6 \) and decreased its mobility within the films. The electrochemical experiments demonstrated that the permeation of the films in the hydrated states could be adjusted by altering the cross-linking degrees within the films.

3.4. Molecule Loading and Release of Cross-Linked Films. Inspired by the varying permeations of the films with varying cross-linking degrees, we wondered whether controlled permeation could be further used to control the release of small molecules. The multilayered films of \((\text{PAH}/\text{PAA})_{6.5}\) with varying cross-linking degrees were first treated in basic solutions and then loaded with fluorescein disodium molecules. We hypothesized that, after treatment with the basic solution, films with varying permutations would be prepared and, as a result, the fluorescein trapped in the film should also be lost to varying extents. The film with the low cross-linking degrees after treatment in basic solutions held the highest amount of fluorescein disodium molecules (Figures 4 and S2) and released the molecular loadings the most rapidly. Over 80% of the maximum release amount of fluorescein sodium was released within the first hour for the film with the low cross-linking degree, and release maximum was reached after approximately 4 h. For the film with the medium cross-linking degree, around 65% of the maximum release amount was released in the first hour, and the release lasted for about 10 h. For the film with the high cross-linking degree, less than 50% of the maximum release was achieved in the first hour, and the release lasted over 10 h. In contrast to the more extended release period for films with higher cross-linking degrees, the maximum release amount decreased with increased cross-linking degrees. These measurement results were consistent with AFM and electrochemical studies that the films with decreasing cross-linking degrees experienced more mass loss during treatment in basic solutions and thus were the most spacious to hold small molecules. At the same time, the lower cross-linking degrees also exerted smaller diffusion barriers toward the held molecules and they diffused into the solution to reach concentration equilibrium faster. Loading and release of the negatively charged Por molecules from the \((\text{PAH}/\text{PAA})_{6.5}\) multilayers were also studied in basic solutions, and the results further supported the notion that the release profile of the incorporated molecules could be effectively adjusted by the cross-linking degrees of the multilayers, as shown in Supporting Information Section 3.

3.5. AuNP Nanoparticle Generated In Situ. The adjustable permeation of the multilayers prompted us to ask whether nanoparticles with varying morphologies could be obtained in these films by coupling the molecular diffusion process with a redox reaction. AuNPs are among the most frequently used nanoparticles because they hold potential applications in a variety of disciplines such as catalysis, sensing, and biomedical engineering. Previous studies reported that AuNP morphologies could be adjusted by varying the reagent addition rates. In our multilayers, the reagents that diffused into or out of the film would have an equivalent effect as adjusting reagent addition rates. We then practiced preparing AuNPs with various morphologies (and thus functions) taking advantage of the varied holding and release efficiencies of the films tuned by the cross-linking degrees in the multilayered films (Figure 5). The multilayered films of varying cross-linking degrees (after treatment in basic solutions) were immersed in a solution of hydrazine hydrate. Immersion in the \( \text{N}_2\text{H}_4 \) solution did not remarkably sabotage film integrity because of the cross-linking which increased film stabilities (Figure S4). Immediately after being lifted up from the hydrazine hydrate solution, the substrates were then immersed into a solution of chloroauric acid, where hydrazine hydrate would diffuse out of the film and, simultaneously, chloroauric acid into the film driven by concentration gradients. The reaction between hydrazine hydrate and chloroauric acid took place quickly at ambient temperatures (25 °C), and the diffusion speed and reaction rate collectively determined the density and morphologies of the
generated nanoparticles, according to the chemical formula (1).29,30

\[ 4\text{AuCl}_4^- + 3\text{N}_2\text{H}_4 + 12\text{OH}^- = 4\text{Au} + 3\text{N}_2 + 12\text{H}_2\text{O} + 16\text{Cl}^- \]  

(1)

These generated gold clusters presented dimensions in the nanoscopic scale and presented catalytic and signal enhancement activities (Figure 5b,d). Interestingly, SEM images indicated that the composite film prepared from the multilayer with the medium cross-linking degree displayed the most abundant nanoscopic gold particles, and particle aggregates were abundant all over the substrate surface. In contrast, the one prepared with the high cross-linking degree displayed a medium number of nanoscopic particles and particle aggregates were absent, while the one from the low cross-linking degree had the smallest number of discrete nanoscopic particles. These observations could be explained by the interplay of the regulated diffusion speed and the total amount of molecules held in these films. The film with the high cross-linking degrees held the least amount of molecules. Although holding the most amount of small molecules, the one with the low cross-linking degrees lost them very quickly. The film with the medium cross-linking degree held a medium amount of molecules and lost them due to diffusion at the medium speed. When the regulated molecular preservation and diffusion within the multilayered films were coupled with the reaction between hydrazine hydrate and chlorauric acid, film-embedded nanoparticles with varying densities and states of aggregation were obtained.
The varied nanoparticle densities in these films in turn resulted in dramatically different functionalities stemming from the AuNPs. In accordance with the morphological observations, the film with the medium cross-linking degree displayed the highest catalytic and signal enhancement capabilities. The catalytic properties of the AuNP–polyelectrolyte composite films were demonstrated using the classic reaction, the catalytic conversion of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) (2). This reaction has been extensively studied because it holds industrial and environmental significance.

\[
\begin{align*}
\text{OH} & \quad \text{Au} \quad \text{OH} \\
\text{NO}_2 & \quad \text{NaBH}_4 & \quad \text{NH}_2
\end{align*}
\]

(2)

When the substrates covered by the AuNP–polyelectrolyte composite multilayers were inserted into the solution of 4-NP, the color of the solution gradually turned from yellow to colorless, indicating that 4-NP was reduced to 4-AP (Figure S5). The composite film prepared from the polyelectrolyte film with the medium cross-linking degree displayed the highest catalytic rate, and within 20 min, the solutions absorbance rapidly reached its minimum. The composite film prepared from the high cross-linking degree catalyzed with medium efficiency and the absorbance of the solution reached a minimum after 70 min. The one prepared from the low cross-linking degree catalyzed with the lowest efficiency, and the absorbance of the solution hit a minimum only after 95 min. In order to further demonstrate the possible applications of our methodology, we assembled a fluidic catalytic device, as shown in Figure S6f. UV–vis spectra indicated that 4-NP was effectively converted into 4-AP during flow through this device, demonstrating that our method of surface-engineering could be potentially applied in flow catalysis devices.

In addition to catalytic capabilities, the gold nanoscopic particles presented signal enhancement properties. In accordance with the catalytic performance sequence, the composite film prepared from the polyelectrolyte film with the medium cross-linking degree enhances the Raman signal most effectively, probably due to the wide existence of hot-spots in between the particle aggregates. After immersion in a Rhodamin 6G solution of \(10^{-6}\) M followed by lifting up and drying, only the composite film prepared from the polyelectrolyte multilayer with the medium cross-linking degree gave clear Raman signals, leading to an enhancement factor of \(9 \times 10^6\), which was comparable with SERS substrates reported in many previous studies.35,36 Previsouly, the substrate SERS enhancement properties have been obtained using a variety of strategies, including surface assembly of noble metal particles,35–37 generation of noble metal arrays or patterns using nanolithography or imprinting techniques,38,39 and polymer-induced noble metal deposition.40 The SERS substrate strategy proposed herein was achieved via a new mechanism, which is the interplay between simultaneous molecular preservation and release capabilities of the film and the chemical reaction rate to generate noble metals. This method assumes the merits of LbL films which would include being facile, compatible with various substrate geometries, and applicable to large-scale surface engineering.

3.6. Cell Adhesion and Spreading Responses. Finally, because LbL films with controlled release properties have frequently been used as biomedical materials, we studied the influence of cross-linking degrees on cell adhesion and spreading to demonstrate biocompatibilities of the prepared multilayers (Figure 6). Cells adhered and spread on all the multilayers with varying efficiencies, and the film with the high cross-linking degree induced cell adhesion and spreading the most effectively.48 After 4 h of culturing, over half of the cells on the film with the high cross-linking degree had already spread, while the ones on the films with the low and medium cross-linking degrees retained their spherical shapes. After 24 h of culturing, cells completely covered the film with the high cross-linking degree and formed a contiguous cell sheet. On films with the low and medium cross-linking degrees, cells also effectively spread, but vacant areas absent of cells with sizes of hundreds of micrometers were present. These results indicated that the cross-linked multilayered films prepared from our photochemical method possessed high cell compatibility and should be potentially applicable in biomedical materials.

4. CONCLUSION

We have demonstrated that a variety of interfacial properties, including permeation, catalytic capability, signal enhancement properties, and cell adhesion and spreading efficiencies, can be tuned by adjusting the cross-linking degrees of the LbL polyelectrolyte multilayers using a proposed photochemical strategy. We employed the photochemical cross-linking method termed “post infiltration followed by photochemical cross-linking” to prepare LbL polyelectrolyte films. The cross-linking degrees were tuned by varying the infiltration time of the conventionally built multilayers in a solution of photoactive cross-linker, DAS. Films with the low, medium, and high cross-linking degrees experienced varying degrees of mass loss upon immersion in basic solutions. After treatment in the basic solution, the film with the low cross-linking degree showed the highest permeation, and the high cross-linking degree showed the lowest permeation. These variations of the permeation could be further employed in a controlled release or interaction that involves gold nanoparticles with varying densities and morphologies. The composite AuNP–polyelectrolyte films prepared from the medium cross-linking degree presented the highest catalytic and signal enhancement capabilities. In addition, the multilayered film possessed high biocompatibility and the cross-linking degrees also adjusted cell behaviors on top of these films. Cells adhered and spread more efficiently with increasing cross-linking degrees. Because LbL assembly has developed as one of the most widely employed interfacial
engineering methods, we expect that our reported results of the supra-adjustability of film properties by tuning cross-linking degrees will open new possibilities in a wide variety of disciplines including biomedical engineering, smart devices, and functional systems.

**ASSOCIATED CONTENT**

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b10453.

AFM images of the films, loading and release of Por from cross-linked films, solution absorbance during the release of fluorescein disodium, and UV−vis spectra of the solution during the catalytic conversion of 4-NP to 4-AP catalyzed by AuNP−polyelectrolyte film (PDF)

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the NSFC (21301369, 21673209, 51572246), the Fundamental Research Funds for the Central Universities (2652015295), and Beijing Nova Program (Z141103001814064).

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