Supporting Information

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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Figure Captions

FigureS1.AFM image of film before and after treatment in basic solutions for the films with low/medium/high cross-linking degrees. Half of the film was cut off before test.

FigureS2. Loading and release of Por from cross-linked film. a) Schematic illustration of Por-incorporated multilayers. b) Film absorbance at 408 nm versus immersion times in a basic solution of pH 11.5. Film absorbance after varying immersion periods for the multilayers of c) low, d) medium, and e) high cross-linking degrees. In panel C, the absorbance curves between 3 min and 150 min overlapped.

FigureS3. Solution absorbance during the release of fluorescein disodium versus release time in equilibrium with $(PAA/PAH)_{6.5}$ films with the low/medium/high cross-linking degrees.

Figure S4. Normalized film absorbance intensity at 340 nm for films with low (a), medium (b), and high (c) cross-linking degree (after treatment in the solution of NaOH) upon immersion in the solution of N_2H_4 (8 wt%), plotted against immersion time.

FigureS5. Solution absorbance during the catalytic conversion of 4-NP to 4-AP catalyzed by AuNP-polyelectrolyte film prepared from multilayers of the (a) low, (b) medium, and (c) high cross-linking degrees.

1. AFM cross-section images of the LbL films before and after basic treatment.

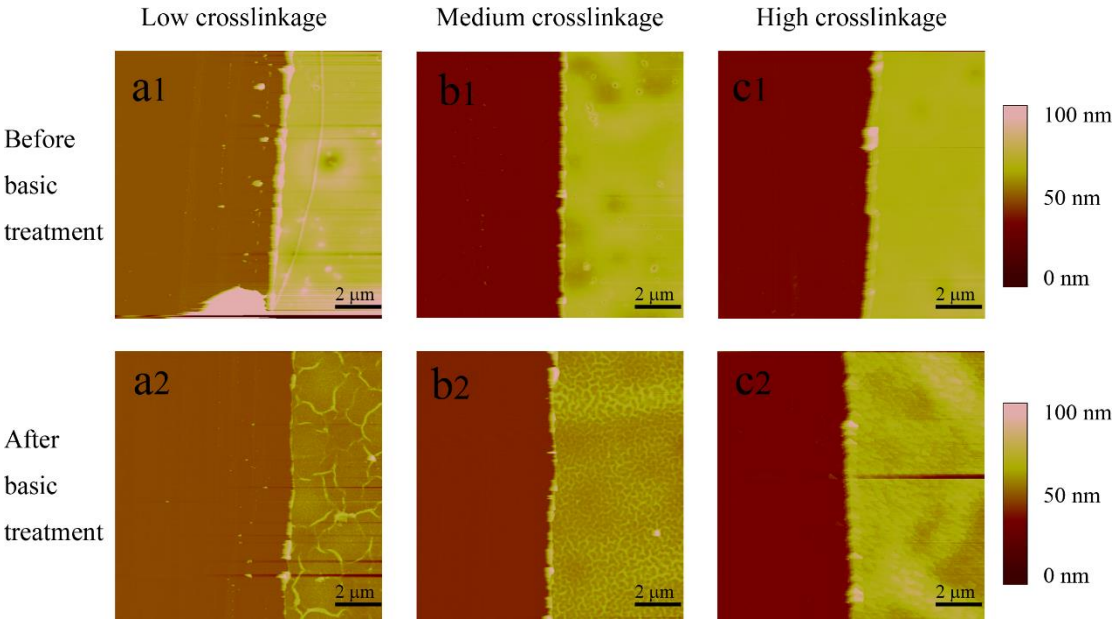

Figure S1.AFM image of film before and after treatment in basic solutions for the films with low/medium/high cross-linking degrees. Half of the film was cut off before test.

2. Solution absorbance during the release of fluorescein disodium

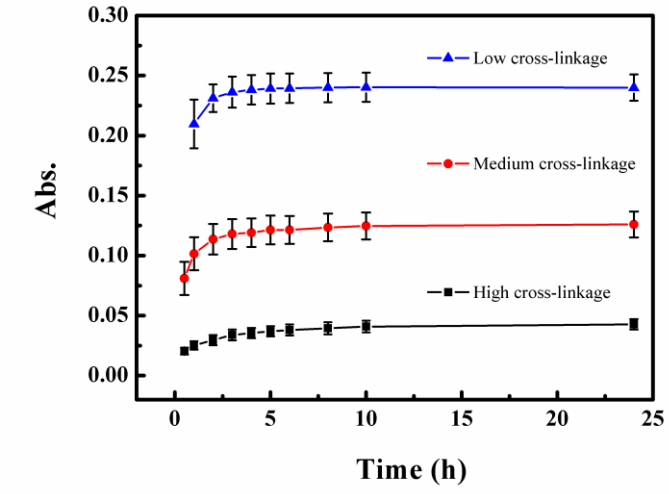

Figure S2. Solution absorbance during the release of fluorescein disodium versus release time in equilibrium with $(PAA/PAH)_{6.5}$ films with the low/medium/high cross-linking degrees.

3. Loading and release of Por from the LbL films with varying cross-linking

degrees.

The entrapment of Por is very similar to the assembly of a multilayer. The pretreated quartz substrate was immersed in a solution of PAH (1 mg·mL^{-1}, pH 9.4) for 20 min, washed with water and dried under a nitrogen flow, then the substrate was transferred to Por solution (1 mg·mL^{-1}, pH 7) for 20 min, washed and dried. The process was repeated five times in order to obtain a film composed by PAH and Pro. After that, the substrate was further subjected to the LbL assembly process as described in Section 2.2. During the Por release process, the multilayered film was immersed in a basic solution (pH 11.5) and film absorbance was monitored during the release process.

We studied the release of the negatively charged Por molecules from the $(PAH/PAA)_{6.5}$ multilayers. In these experiments, Por was incorporated into the multilayered films by assembling it with PAH, to generate the multilayers $(PAH/Por)_5$. Subsequently, multilayers of PAH/PAA were prepared as the outmost layers, resulting in multilayered films of $(PAH/Por)_5(PAH/PAA)_{6.5}$. The infiltration of DAS and subsequent cross-linking of the multilayers did not influence the existence of Por in the films. The composite films were then immersed in a basic solution (pH =11.5) for the release experiments, and UV-vis spectra were employed to follow the process of the release, as shown in Figure S3. For the multilayers with the low cross-linking degree, the release of Por was quickly completed within the first 3 min. For the film with the medium cross-linking degree, the majority (85% of the totally released amount) of Por was released within about 10 min. For the film with the high cross-linking degree, the release process was significantly delayed. Around 80% of

totally released amount of Por was released in 30 min, and 90% was released within the first 60 min. In addition, according to the absorbance residue of the rinsed film, the film with the highest cross-linking degree still held the highest amount of Por after an extended period of release experiments. These results indicated that the release profile of the incorporated molecules in basic solutions could be effectively adjusted by the cross-linking degrees of the multilayers.

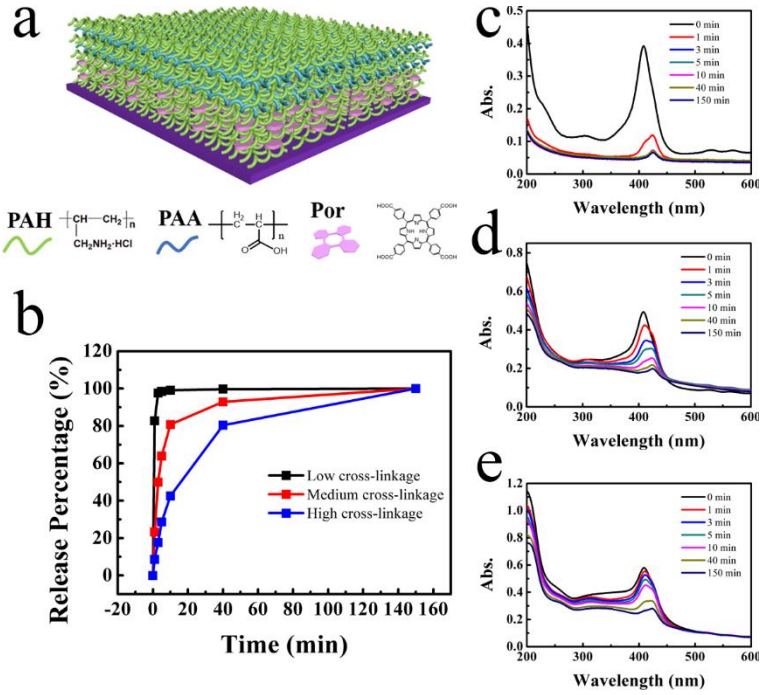

Figure S3. Loading and release of Por from cross-linked film. a) Schematic illustration of Por-incorporated multilayers. b) Film absorbance at 408 nm versus immersion times in a basic solution of pH 11.5. Film absorbance after varying immersion periods for the multilayers of c) low, d) medium, and e) high cross-linking degrees. In panel C, the absorbance curves between 3 min and 150 min overlapped.

4. Film (after treatment in the solution of NaOH) absorbance during immersion

in the solution of N_2H_4.

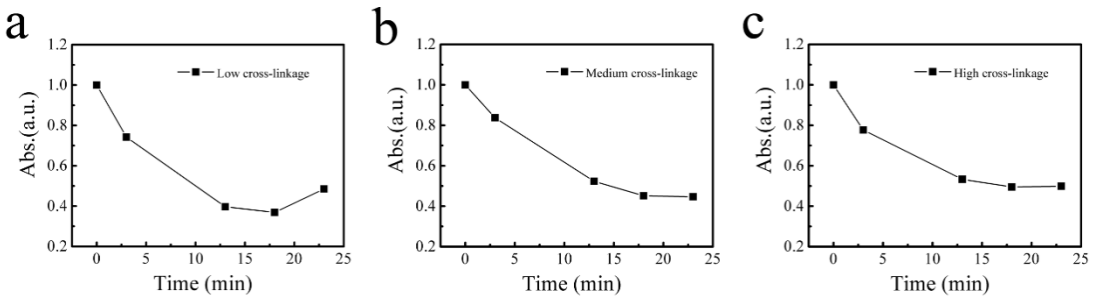

Figure S4. Normalized film absorbance intensity at 340 nm for films with low (a), medium (b), and high (c) cross-linking degree (after treatment in the solution of NaOH) upon immersion in the solution of N_2H_4 (8 wt%), plotted against immersion time.

5. UV-vis spectra of the solution during the catalytic conversion of 4-NP to 4-AP catalyzed by AuNP-polyelectrolyte film

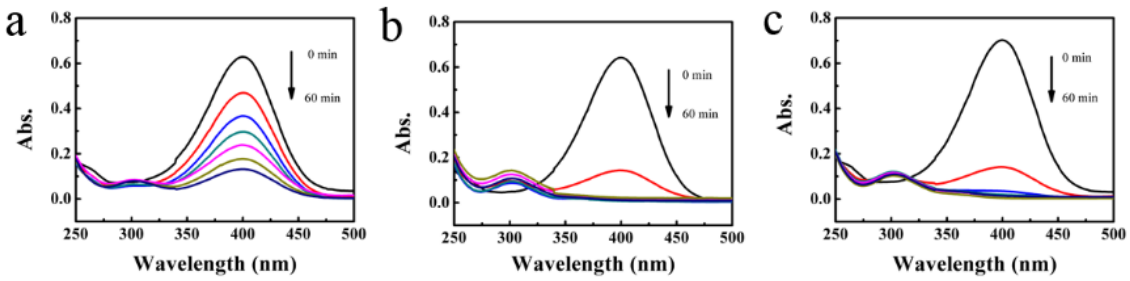

Figure S5.UV-vis spectra of the solution during the catalytic conversion of 4-NP to 4-AP catalyzed by AuNP-polyelectrolyte film prepared from multilayers of the (a) low, (b) medium, and (c) high cross-linking degrees.