SUPPORTING INFORMATION

Silver nanoparticle aided self-healing of polyelectrolyte multilayers

Xiayun Huang,[1] and Nicole S. Zacharia[1,2]*

[1]Dept. of Mechanical Engineering, Texas A&M University, College Station, TX 77843, [2]Dept. of Polymer Engineering, University of Akron, Akron, OH 44325.

*Correspondence to: nzacharia@uakron.edu

Supplementary materials:

Supplementary Figures S1-S2

Supplementary Movies S1-S2

The growth curves of polyelectrolyte multilayer films.

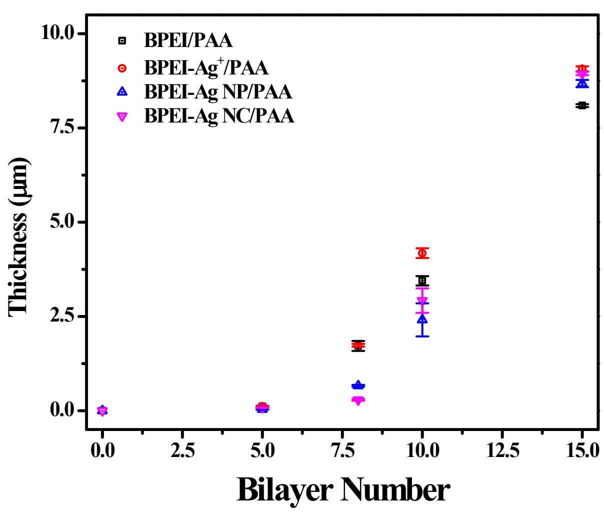

Fig. S1 The growth curves of polyelectrolyte multilayer films. (a) BPEI/PAA, (b) BPEI-Ag+/PAA, (c) BPEI-Ag NP/PAA and (d) BPEI-Ag NC/PAA. The initial 15 bilayers of multilayer film grow exponentially.

Fig. S1 shows a magnification of the first 15 bilayers of the growth curve for the polyelectrolyte multilayer films from figure 1, exhibiting exponential growth. All of these film follow the exponential growth during the first 15 bilayers, following the “in and out” diffusion mechanism.

TEM image of Ag nanoclusters and Ag nanoparticles

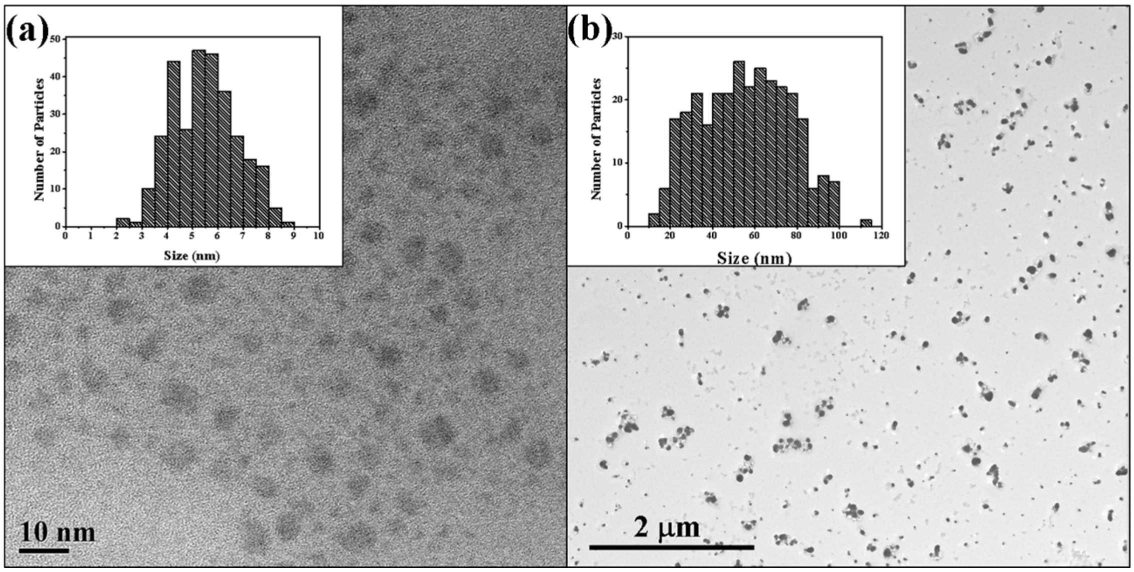

Fig. S2 TEM images of (a) Ag nanoclusters and (b) Ag nanoparticles embedded in the PEMs. Insert images were the respective histogram of 300 silver particles measured in different area. The size of nanocluster was 5.5 nm±1.3 nm, while that of nanoparticles was 54.8 nm±21.1 nm.

Here, we introduced two different sizes of Ag particles embedded into the PEMs to investigate the difference in healing properties. The TEM images of Fig. S2 show the size and related distribution of Ag nanoclusters and Ag nanoparticles. The size of these would be 5.5nm±1.3 nm and 54.8 nm±21.1 nm, respectively. The size and histogram were collected by 300 different particles from different areas and measured as diameter of particles.

FTIR spectra of polyelectrolyte multilayer films

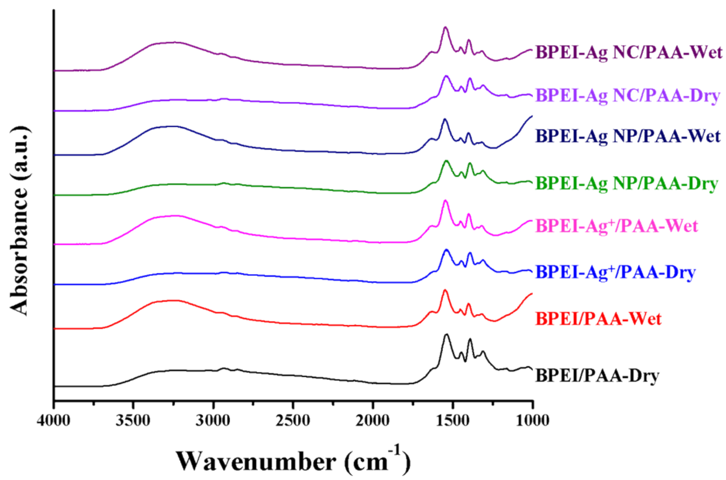

Fig. S3 FTIR-ATR spectra of dry and wet film of BPEI/PAA, BPEI-Ag^+/PAA, BPEI-Ag NP/PAA, and BPEI-Ag NC/PAA. There are not distinguishable difference with Ag^+, Ag NP or Ag NC.

Fig. S3 shows the FTIR-ATR spectra of the dry and wet film of BPEI/PAA, BPEI-Ag^+/PAA, BPEI-Ag NP/PAA, and BPEI-Ag NC/PAA. The dried BPEI/PAA film has the high absorbance of deprotonated carboxyl group (-COO^-) at 1541 cm^{-1} compared with protonated carboxyl group (-COOH), which should be around 1710 cm^{-1}. The shoulder peak around 1640 cm^{-1} is from the amine groups from BPEI. Once BPEI/PAA film was immersed in neutral water, a broad OH stretch at 2900-3400 cm^{-1} immediately appears. However, other peaks did not shift or change relative intensity distinguishably. Adding Ag^+, Ag NP or Ag NC into the BPEI/PAA multilayer film also did not change the FTIR-ATR spectra and therefore does not change the degree of ionization of BPEI and PAA in the film appreciably.

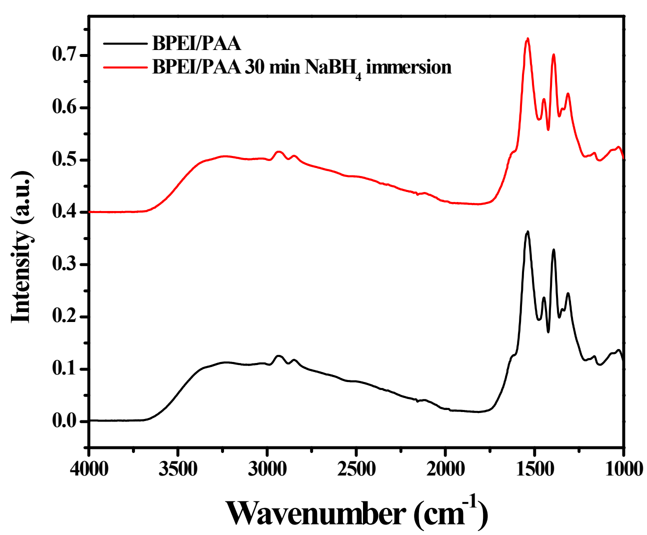

Fig. S4 FTIR spectra of 30 bilayer BPEI/PAA dry (black) and BPEI/PAA film after immersing in 10 mmol/L $NaBH_4$ aqueous solution for 30 min (red). From the FTIR spectra there cannot be seen any difference in the films caused from immersion in $NaBH_4$.

FTIR spectra (figure S4) of a BPEI/PAA without any silver before and after exposure to $NaBH_4$ solution shows no appreciable change, from which we can conclude that no chemical changes are taking place in these films.

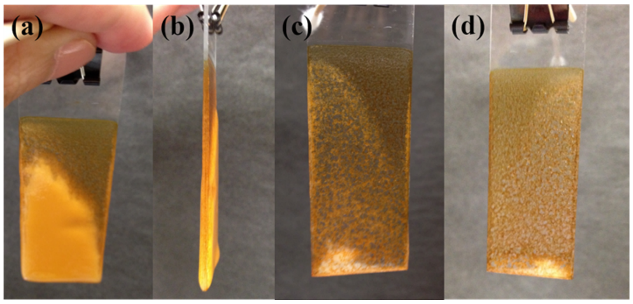

Fig. S5 The water swelling of 30 bilayers BPEI-Ag NP/PAA films. The front view (a) and side view (b) of film immerse in the water for 10 hours. Top part of the film start to show this porous features and the bottom part was still in the swelling state. The porous feature extended from top to bottom to the whole film with time going on. (c) Film immerse in the water for 30 hours water immersion. Part (d) the porous features remain in the dried film.

Over long soaking times (tens of hours) it can be seem that the film containing Ag NPs are not stable, forming pores over tens of hours, seen in figure S5. This restructuring of the film is not happening over the 10 – 15 minute healing times we investigate here. FTIR spectra, fig S6, show that after soaking the film for 48 hours in neutral water, a small amount of polyelectrolyte seems to have left the film.

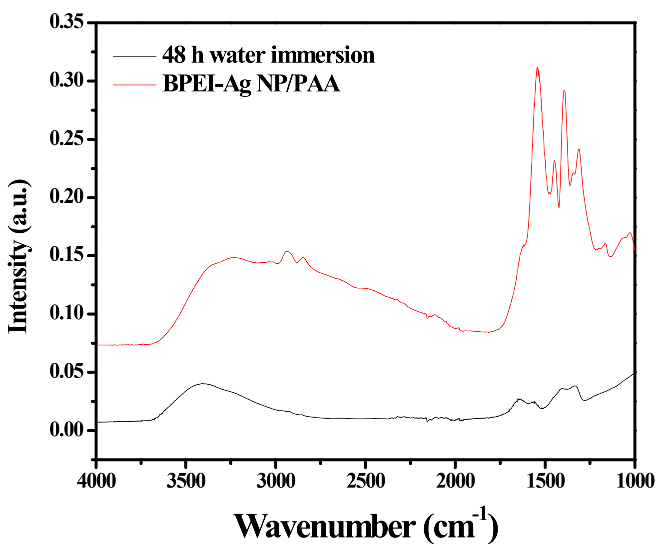

Fig. S6 FTIR spectra of 30 bilayer BPEI-Ag NP/PAA dry (red) and residues diffused from the film into water (black) after film immersed in the film for 48 hours.

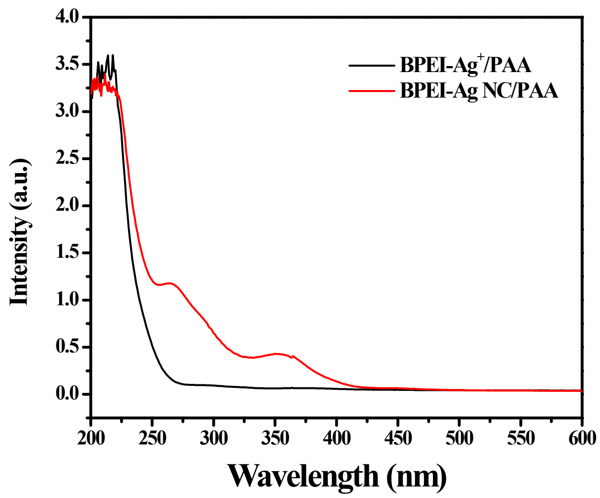

Fig. S7 UV-vis spectra of BPEI-Ag+/PAA films (black) and BPEI-Ag NC/PAA (red), both on quartz slides, showing the evolution of the orange-brown color that is the surface plasmon resonance of the newly formed nanoclusters.

Figure S7 shows the UV-vis spectrum of the BPEI-Ag+/PAA film, which has no appreciable features, and then the spectrum of the film with Ag NPs which has an orange-brown color.

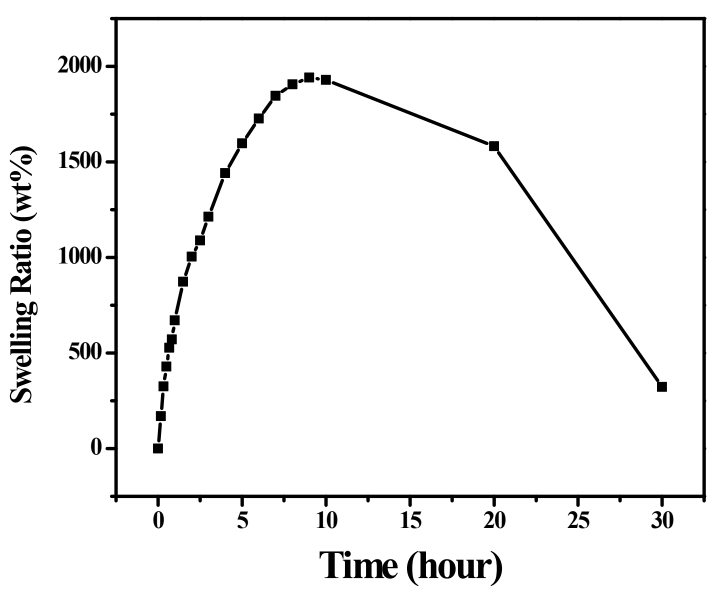

Fig. S8 The swelling ratio of 30 bilayers BPEI-Ag NP/PAA films immersed in the water for different time periods

Figure S8 shows how the Ag NP containing film takes up water for some time period and then starts to reduce in mass as pores are being formed.

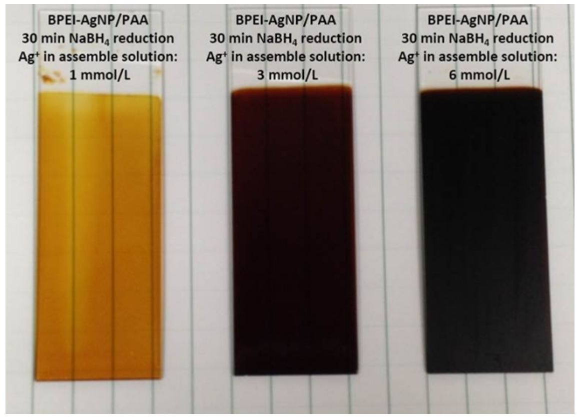

Fig. S9. Images of BPEI-Ag NP/PAA films assembled with different Ag+ ion concentrations in the BPEI assembly solution; from left to right 1 mmol, 3 mmol, and 6 mmol.

Figure S9 shows the difference in color amongst the films containing 1, 3, and 6 mmol of Ag+ ion in the BPEI dipping solution. The films are darker with increasing silver content and rougher as well.

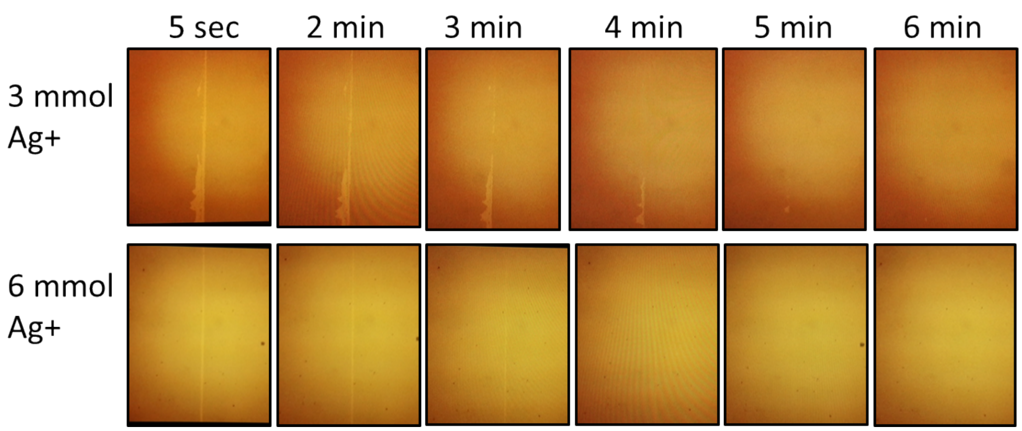

Fig S10. Top row depicts time lapsed images of a film assembled with a 3 mmol Ag+ ion concentration healing, and the bottom row depicts the same for a film assembled with 6 mmol Ag+ ion concentration.

Figure S10 shows images from the healing process for films assembled with higher concentations of silver ion. The healing process seems to be completed at nearly the 5 minute mark in both cases; for the 3 mmol case there were larger features in the scratch that still had not healed at 5 minutes but were nearly completely gone at 6 minutes. With this qualitative observation it is not possible to say that there are difference between the two cases, but these two films heal more quickly than the 1 mmol case, as can be seen by comparing the movie S1 to these stills.

Movie S1 Self-healing property of in-situ optical microscope movie of BPEI-Ag NP/PAA film

Movie S1 shows the real-time motion of BPEI-Ag NP/PAA film re-healed within 10 min. An optical microscope (VHX-600, Keyence Co.) was used as in-situ observation of the healing properties with long working distance and wide depth of field lens (VH-Z100). The lens used in this in-situ observation was the same as the one used for images in fig. 3 and fig. 4.

Movie S2 Self-healing demo movies of BPEI/PAA, BPEI-Ag^{+}/PAA, BPEI-Ag NP/PAA and BPEI-Ag NC/PAA film healed with each other with water spray.

The videos and pictures in the movie S2 were taken with a Canon EOS REBEL T3i by Sin Dik (Cindy) Ma. The video was made of two separate videos which had original frame rates of 29 frames per second and a total bit rates of 47187kbps and 48019kbps. The final version of the video has a frame rate of 22 frames per second and 1128 kbps.

Movie S2 shows the re-healing properties of the free standing film. These four kinds of free-standing films were deposited, peeled from polystyrene plate and cut as 1cm×1cm. Let these free-standing film attached with each other in the order of BPEI/PAA, BPEI-Ag^{+}/PAA, BPEI-Ag NP/PAA and BPEI-Ag NC/PAA film from left to the right and spray with water. After dried for 2h, the film could be peeled off from the polystyrene substrate as one film but still shows each piece clearly.