Amine Functionalization of Silica Sol–Gel Thin Films via Kinetic Doping: A Novel, Green Approach

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Supporting Information

ABSTRACT: Amine-functionalized thin films are highly desirable technologies for analytical, material, and biochemistry applications. Current functionalization procedures can be costly, environmentally unfriendly, and require many synthetic steps. Here, we present an inexpensive and facile way to functionalize a silica thin film with a 25,000 MW branched polyethylenimine (BPEI), consistent with green chemistry principles. Using UV−vis spectroscopy and scanning electron microscopy, BPEI was determined to be loaded into the film at an approximately 0.5 M concentration, which is a 500× increase from the loading solution used. The films were also tested for copper(II) sequestration to assess their potential for heavy metal sequestration and showed a high loading capacity of 10 ± 6 mmol/g. Films proved to be reusable, using ethylenediaminetetraacetic acid to chelate copper and regenerate the films, with only a 6% reduction in the amount of copper(II) ions sequestered by the third use. The films also proved stable against leaching over the course of 1 week in solution, with less than 1% of the original BPEI lost under various storage conditions (i.e., storage in deionized (DI) water, storage in dilute BPEI solution, storage in DI water after annealing). These films show promise for multiple applications, from heavy metal sequestration to antifouling applications, while being inexpensive, facile, and environmentally friendly to synthesize. To our knowledge, this is the first time that BPEI has been doped into silica thin films.

INTRODUCTION

Surface functionalization of silica is of great interest in many different fields, with the ability to change the surface chemistry of silica particles, monoliths, and thin films, and is a highly desirable technology. Functionalization can drastically change the behavior of the silane groups that are typically found on the surface of silica gels.1−5 Surface functionalization of silica with various amine-containing compounds has shown increased adsorption of proteins,6 antifouling effects,7 increased heavy metal adsorption,8 chromatography applications,9 catalytic applications,10 and more.

One polyamine of great interest for the functionalization of silica solid substrates is branched polyethyleneimine (BPEI). BPEIs are polymers of variable molecular weights and rich in primary, secondary, and tertiary amine groups. They have shown great potential for environmental applications such as aqueous heavy metal removal11,12 and carbon dioxide capture13 when attached to a solid substrate. They have also shown antimicrobial activity both on their own14 and as antibiotic potentiators.15

While BPEI has been loaded into monoliths and nanoparticles, to the best of our knowledge, they have never been successfully loaded into silica thin films, most likely due to their very basic nature that may significantly impair thin-film formation.16 Thus, there is a distinct possibility that the incorporation of BPEI may adversely influence the structural integrity of a sol–gel thin film. Amine-functionalized thin films present expanded application possibilities, such as antifouling coatings or coatings for heavy metal remediation.

To this end, many authors have employed multiple synthetic steps often with environmentally harmful organic precursors or solvents,17−19 and there is much interest in developing more generic, robust, and “green” technologies where the reduction in the usage of harmful solvents is strongly encouraged.20,21 Kinetic doping utilizes aqueous solutions for loading the BPEI guest molecules into silica thin films, eliminating the need for any organic solvents relative to other competing surface functionalization technologies.17−19 Using aqueous solutions with low concentrations of BPEI to functionalize silica thin films, the need for environmentally hazardous solvents to generate precursors or perform postcoating surface modification can be effectively eliminated, resulting in a much more green technique.

Silica thin films with amine functionalization can be made with organosilane precursors that contain an amino-functional...
group, but this limits the size of the amine groups that can be introduced into the film. Additionally, every new amine compound requires the synthesis of a new organosilane precursor, adding another layer of complexity to the functionalization process. Amine-containing polymers alone can be used to create thin films, but they lack the benefits of silica, like high surface areas, and many exhibit poor stability in water. Plasma polymerization can be used to graft amine groups onto existing thin films, but the high cost of plasma polymerization is prohibitive to widespread commercial applications. It is possible to functionalize silica thin films with polyethylenimine, as certain synthetic pathways have been demonstrated to functionalize the surface of silica gels, but they require multiple steps and environmentally hazardous chemicals. Here, we present a facile, inexpensive synthesis of silica sol–gel thin films with doped BPEI that provides amine functionalization with high loading efficiency using relatively green chemistry principles.

Doping of BPEI into a silica sol–gel thin film, instead of synthetic functionalization of the surface, would allow for a facile, green synthesis with very few synthetic steps involved. However, polymers with high molecular mass present a challenge for both the traditional pre- and postdoping approaches to thin-film loading, as too much polymer included in predoping, which is a technique that introduces dopants to the sol before depositing the film on a substrate, will likely degrade the structural integrity of the resulting silica film. Whereas due to poor diffusion, a high-molecular-weight polymer is never an ideal candidate for postdoping, which involves adsorbing the dopant to porous surfaces, due to poor diffusion. Kinetic doping is a technique for loading guest molecules into sol–gel thin films that involves introducing guest molecules into a still-evolving film, allowing them to be entrapped by the growing silica network. This technique is well suited to overcome the challenges posed by BPEI to the more widely used doping techniques. Additionally, kinetic doping has previously been studied with positively charged organic dyes and enzymes as the dopant molecule, making BPEI, with its organic nature and high positive charge density at neutral pH, an ideal candidate for kinetic doping.

Here, we attempt to dope silica sol–gel thin films with 600 and 25 000 MW BPEI. Using scanning electron microscopy (SEM) and UV–vis spectroscopy, the quality of the thin films and the amount of doped BPEI were quantified. The resultant films are structurally sound with BPEI concentrations in the range of 10 mmol of copper(II) ions per gram of film from solution, an approximately 5-fold or more increase over most available amine-functionalized gel preparations.

Soaking in ethylenediaminetetraacetic acid (EDTA) solution in a subsequent step can remove these ions, regenerating the film that can be reused, with only a 6% decrease in copper(II) ion sequestration efficacy after three uses. This lends preliminary support for the use of these films in heavy metal removal with good reusability. It is also, to our knowledge, the first time that BPEI has been loaded as a guest molecule in silica sol–gel thin films.

**RESULTS AND DISCUSSION**

**Optimal Loading Parameters for Branched Polyethylenimine (BPEI).** As shown in previous studies, there are several loading parameters that need to be examined for optimal kinetic doping. Film thickness and delay time (the time between the end of drain coating and the introduction of the film to the loading solution) are important factors that influence optimal loading. Dopants that do not disrupt film structure have been shown to have an optimal delay time of 5 min for drain coating. This may be different for BPEI, as the extent of polycondensation of the silica network increases with the delay time. Due to its basic nature, BPEI may load better into a thin film that has different levels of condensation than dopants that are relatively neutral. Drain speed can change the thickness of the film and possibly the absolute amount of BPEI loaded into the film. The film must be thick enough to quantify the amount of BPEI loaded, as thicker films are expected to host more BPEI molecules. Too thick films will lead to increasing thickness variations across the film, due to the forces that dominate drain coating in the high-speed regime.

Two molecular weights of BPEI, a lighter 600 MW and a heavier 25 000 MW, were tested to determine if identical loading parameters would work for BPEI with different molecular weights. They were tested as BPEI of different sizes are known to react differently with many different chemicals, including silica.

**Molecular Weight.** BPEI is a polymer that comes in many molecular weights. Different molecular weights have different properties; for example, the cytotoxicity of BPEI increases with increasing molecular weight. Thus, it is desirable to explore the possibilities to produce silica films with BPEI of different molecular weights, hence with different cytotoxicities. Consequently, the loadings of both a low- and a high-molecular-weight, 600 and 25 000 MW, BPEI were attempted. However, none of the parameters that were tested, including drain speed, delay time, and pH of the loading solution, could be optimized to allow the kinetic doping of the 600 MW BPEI. Any attempt to load within the kinetic doping window led to complete film destruction and visible silica particle aggregates formed in the solution. It was possible to load the higher molecular weight, 25 000, and loading parameters for that weight were further refined.

BPEI and tetraethyl orthosilicate (TEOS) are known to form nanoparticle, which may act as undesirable competing process with the kinetic doping of BPEI into silica thin films, the speed of which seems to vary with varying molecular weight. Kinetic doping is thought to work because the polycondensation of the liquid sol is still progressing during the doping stage and the dopant can still be entrapped by the evolving and growing silica network. The only films that stayed intact upon contact with the 600 MW BPEI loading solution appeared to have passed this window of doping opportunity and did not allow much loading of the 600 MW BPEI, despite the smaller molecular weight. Different molecular weights of branched or linear polyethylenimines are known to react with silicon sources differently; so, this difference in behavior is not entirely unprecedented. We postulate that this is due to the chemical reaction between BPEI and the TEOS molecules that have not undergone polycondensation. Based on experimental evidence, 600 MW BPEI is likely to react more quickly than 25 000 MW BPEI, so quickly that it outcompetes the polycondensation reaction so that kinetic doping is effectively inhibited.

The observation that different molecular weights of BPEI react with the film differently may prove to be a useful way to control film properties once BPEI of other molecular weights is thoroughly examined. A thorough investigation of the effect of
different BPEI molecular weights on kinetic doping is currently underway.

**Drain Speed.** Film thickness was qualitatively examined for its effect on the mechanical stability of the film and the amount of BPEI that remained solvent-accessible. Thicker films, created with faster drain speeds, take longer to complete the evaporation process that is responsible for the growth of a three-dimensional (3D) network through the polycondensation reaction to produce a mature thin film. Although a thicker film allows more entrapment of BPEI, the slower evaporation process means more uncondensed TEOS molecules remain to undergo undesirable side reactions with BPEI. Films that are too thick will additionally drain-coat in a different regime, leading to increasing thickness variations on the surface of the film itself.35

Figure 1 shows a series of films that were loaded with a delay time of 5 min. To vary the film thickness, films were prepared with drain speeds from 0.67 to 1.50 cm/s; all film coatings were completed in less than 4 s, regardless of the drain speed. Thinner films (those coated at a lower drain speed) showed relatively poor loading of BPEI. As the drain speed increased, the loading became more apparent as indicated by the more intense blue color on the thin film due to complex formation with copper(II) ions. It is also apparent that the highly loaded films exhibited a more significant mechanical deformation at the corner and edges of the film. A drain speed of 1.36 cm/s was chosen for further testing as it resulted in a very visible amount of loading with the least amount of mechanical disruption at the edge.

**Delay Time.** Delay times in drain coating affect the extent of polycrystallization in the thin film when it is introduced to the dopant.35 A less evolved silica network can entrap guest molecules more effectively as more uncondensed TEOS is available to grow around the dopant. However, that same uncondensed TEOS can also react with BPEI and prevent the growth of the silica network into a stable thin film. Indeed, testing of delay times showed that longer delay times produced more mechanically sound films with noticeably less pronounced corner and edge deformation, supporting the notion that BPEI reacts with TEOS in the films that have not completed condensation. Figure 2A shows the results of loading BPEI with a variety of delay times from 5:00 to 7:30 min and a 1 mM BPEI loading solution. Figure 2B shows a film with a 5:00 min delay time. There are notable structural defects in the film, mostly around the corner and edges of the film and especially on the lower right corner, where a portion of the film was clearly detached from the glass coverslip and subsequently washed away. Figure 2C shows a film with a delay time of 7:30 min. Structural defects in the film are less notable at this longer delay time. Delay times beyond those illustrated in Figure 2 were also tested (8:00, 8:30, and 9:00 min can be found in the Supporting Information), but they progressively produced less loading, despite showing improved mechanical stability over the 7:30 min delay film. This seems to indicate that the kinetic doping window is closing, as very little uncondensed TEOS remains to effectively entrap the BPEI. On the other hand, the more condensed silica network in the longer delay time films seems to better resist the mechanical disruption caused by BPEI, due to the very same lack of uncondensed TEOS.

Thicker films and shorter delay times seem to favor the competing process of nanoparticle formation with TEOS molecules that have not completed condensation, resulting in more severe mechanical defects. This is further supported by the results with the 600 MW BPEI, where silica particle formation outcompeted kinetic doping at all delay times we examined. Thinner films and longer delay times allow the film to reach a higher level of condensation and develop sufficient mechanical strength whereupon, when it is introduced into the basic BPEI, it has built sufficient scaffolding to stay structurally

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**Figure 1.** Films loaded with a 1 mM BPEI loading solution, a delay time of 5 min, at various drain speeds. (A) Films drained at each different setting on the pump from 2 to 10. This corresponds to speeds of 0.67, 0.78, 0.87, 0.99, 1.10, 1.17, 1.25, 1.36, 1.41, and 1.50 cm/s, respectively. Mechanical disruption can be seen most clearly on the corner that is first in contact with the BPEI loading solution (see Figure 6) and on the edges of the films nearest that corner. (B) Close-up of the slowest drain speed film, showing a very faint visible blue color and very little mechanical disruption. (C) Close-up of the final chosen drain speed (1.36 cm/s), showing a more intense visible blue color, but at the expense of more mechanical disruption at the corner and edges.

**Figure 2.** Films loaded with a 1 mM BPEI loading solution, at a 1.36 cm/s drain speed, with varying delay times in triplicate. (A) Delay times ranging from 5 min (top row) to 7 min and 30 s (bottom row), in 30 s increments. (B) Close-up of one of the 5 min delay time films, showing the large mechanical defects caused by the early introduction of BPEI, especially on the lower right corner. Part of the film at the lower right-hand corner was obviously removed during the washing step, as it had detached from the substrate. (C) Close-up of one of the 7 min 30 s films, showing a much less mechanical disruption than the shorter delay time periods but with a slightly lower loading capacity as indicated by the fainter blue color.
sound on the macroscopic level, unfortunately at the expense of BPEI loading. The dopant solution for the thin concentration of the remaining BPEI. The di was then combined with copper(II) chloride to quantify the amount of BPEI loaded for the preloading solution. The average number of moles of BPEI loaded for the preloading solution was taken as the amount of BPEI loaded. Figure 3 shows the absorption spectra of six replicates and the preloading solution. The average number of moles of BPEI loaded for films with a 7:30 min delay time, a 1.36 cm/s drain speed, and a 1 mM dopant solution was 0.7 ± 0.2 μmol. To then calculate the concentration of BPEI in the films, the thickness of the film was measured via SEM.

Quantification of Doped BPEI in Thin Films. The molarity of the doped BPEI was examined using a method based on Wen et al. A standard curve was constructed using a varying amount of BPEI to complex with a constant 1 mM copper(II) solution. This standard curve showed high linearity and an extinction coefficient of 429 mM⁻¹ cm⁻¹ (see the Supporting Information). The dopant solution for the thin films, diluted to the linear range of the 276 nm standard curve, was then combined with copper(II) chloride to quantify the concentration of the remaining BPEI. The difference between the concentration of the solution prior to loading (preloading) and after loading was taken as the amount of BPEI loaded. Figure 3 shows the absorption spectra of six replicates and the Films 1−6 are loading solutions from individual films, where the film was removed after 1 week of loading and the solution left was tested for BPEI concentration.

Scanning electron microscopy (SEM) images were obtained via a JEOL JSM-880 instrument with a 5 nm Au−Pd sputter-coated layer to examine the morphology of the drain-coated thin film and measure the film thickness. Thirteen separate films were examined, 6 with 1 mM dopant solutions and 7 without any loaded BPEI. It was observed that the thickness of the film was highly variable over a single film. Films with BPEI had a wider range of thickness from as low as 53 nm up to 1.93 μm on one film, as can be seen in Figure 4. This seems to partly be a result of the drain coating setup, as a slightly lower variance was seen in the unloaded films, with thicknesses ranging from 1 to 1.79 μm in a single film. The angle of loading in both drain and dip coating is known to affect the thickness and shape of the resultant film, which is not a perfect 90° in our drain coating apparatus. An angle other than a perfect 90° between the substrate and the surface of the liquid sol results in a film with a wedge-shaped, linearly changing thickness across the direction of coating and could explain some of the variances seen. Additionally, drain coating at high drain speeds, like those used for our films, can result in varying thickness across a single film, also contributing to the shape seen in the SEM images. A diagram of the drain coating setup is depicted in Figure S, with the loading angle of the film labeled. The variance across the film in both the loaded and unloaded films suggests that both the angle and drain speed contribute to the thickness variation. While a commercial dip coating setup may enable a perfect 90° angle of loading, the drain speed would have to be lowered drastically to enter the coating regime that might produce a film with even thickness. The resultant film would be too thin for our desired high-capacity BPEI loading.

However, it is important to note that the variance across films loaded with BPEI was consistently much greater. This is most likely due to the interaction of BPEI with the film. The SEM images seem to suggest that the interaction with BPEI causes the edges of the film to thin, but most of the middle portion stays intact. The edges of the film are where BPEI first comes into contact with it (see Figure S). PEI is known to etch silica nanoparticles; so, this may be a similar phenomenon at the edges. This potential etching does not extend to the majority of the film, which remains at the same thickness as the unloaded films. However, given this variance in thickness, only an approximation of the final molarity of the film can be made. If we use an average thickness of 1 μm across the film, the average molarity of the loaded BPEI would be ~0.5 M, an approximately 500× increase over the loading solution; 0.5 M is in line with concentrations previously reported with kinetic doping, but is a lower percent increase over the loading solution than achieved with proteins or rhodamine 6G (R6G) dye. This is most likely due to the competing reactions of...
silica/BPEI particle formation and kinetic doping. The dyes and proteins do not have any competing reactions, meaning all molecules that enter the film should stay there, in their original state, unlike BPEI. In addition, R6G is capable of hydrogen bonding with small pores inside the silica network to further enhance its loading relative to that of BPEI. Nevertheless, the increase in the molarity of the film over the loading solution still means that the very dilute solutions of BPEI can be used to make more concentrated films, reducing the need for larger amounts of BPEI, the most expensive chemical used for producing these films.

Additionally, the SEM images were compared to identify any morphology differences between the BPEI loaded and unloaded films. Figure 6 shows a cross-sectional and top-down image of a loaded film, while Figure 7 shows the same for an unloaded film. The morphology does not seem to change drastically in the cross-sectional images between the loaded and unloaded films, but the grain size seems to be slightly larger in the loaded versus the unloaded films. The top-down view does show noticeable differences: the film surface in Figure 6C appears to be much smoother and devoid of major dents relative to that shown in Figure 7C, suggesting that BPEI does alter the surface morphology of the films to a certain degree. The surface of the film in Figure 7C, the unloaded film, has both small and large “dimples”, with an orange peel effect texture on the surface. Figure 6C, the loaded film, does not show this texture, and the bright spots are only glass fragments. The samples must be cut down to fit in the SEM instrument, causing some glass fragments to appear in the sample images due to the glass coverslip the films are coated on.

Figure 8 also compares an unloaded film to a loaded film, showing dark patches or a “mottled” effect on the SEM image of the loaded film that is most likely due to the presence of BPEI. This mottled effect occurs on all BPEI loaded samples, but none of the unloaded samples, suggesting that it is due to the interaction of BPEI with the electron beam. It is unlikely to be simply organic contamination, as it does not show the characteristic dark square that is the hallmark of hydrocarbon contamination.4 If these darker patches on the SEM images are indeed caused by BPEI, this suggests that the BPEI is distributed fairly evenly throughout the entire thin film, not just localized on the surface. Elemental analysis through energy-dispersive X-ray spectroscopy was attempted to confirm this, but the signal from the glass coverslip substrate was so dominant that no discernible signal was observed for the thin films for a meaningful determination of elemental composition.

Stability of BPEI in Doped Films. BPEI-doped films were tested for leaking over the course of 1 week. Films can be stored dry with no degradation and show no leaking when tested in a copper(II) solution for up to 2 h, but more advanced applications, like heavy metal remediation or anti-biofouling coatings, may require films to be submerged or stored wet for an extended period of time. To test the leaking of BPEI, films were (i) untreated and stored in deionized (DI) water, (ii) annealed at 100 °C for approximately 18 h and stored in DI water, or (iii) untreated and stored in a 0.01 mM BPEI solution. Untreated films in DI water were expected to release the most BPEI, while untreated films in a dilute BPEI solution were expected to release less BPEI due to the reduced concentration difference between the film and the storage solution. Annealed films were also expected to release less BPEI due to morphological changes induced by the annealing process. Annealing is expected to cause silica pore collapse, making it more difficult for BPEI to leave or leach from the film. The results of this study are summarized in Table 1. Over the course of 1 week, the untreated films stored in DI water show the most loss, with a 0.6% loss of BPEI. Storing the films in a 0.01 mM BPEI solution, even without treatment, decreases this loss to 0.4%. Annealing the film further reduces this loss, even when stored in DI water, to 0.1%. Collectively speaking, these results suggest that BPEI-doped films could be used for an extended period of time in solution.
Copper(II) Uptake and Reusability. Copper(II) ion uptake by the films was tested to obtain preliminary data on the suitability of this technology for heavy metal remediation. On average, films were able to sequester 10 (±6) mmol of copper ions per gram of film. In comparison, the best commercial resin documented so far for copper(II) uptake is 2.06 mmol/g.31 Our thin film also outperforms newer, more expensive ion imprinting technology, made with an amino-functionalized silane precursor, with our copper(II) loading capacity an order of magnitude higher than that reported (39.82 mg/g or ∼0.6 mmol/g) and with comparable regeneration capabilities.12,45 The film also outperforms several other technologies that use (B)PEI; a PEI/silk fibroin hydrogel has a copper(II) uptake of 163.9 mg/g (∼2.6 mmol/g),46 silica-bound BPEI has a copper(II) capacity of less than 5 mmol/g,32 and even a PEI-functionalized ion-imprinted hydrogel had a similar uptake to the other hydrogels cited (40.00 mg/g or ∼0.6 mmol/g).32

This enhanced uptake per mass makes sense, as the resin or bulk materials are likely only able to sequester ions on the surface, whereas most of its bulk remains inaccessible to metal ions. According to our SEM data, BPEI is likely loaded throughout the film, and much of it is expected to be accessible to the copper(II) ions, due to the highly porous nature of silica versus the other polymers that have been used, making it highly efficient at sequestering metal ions from solution. Additionally, the concentration of BPEI loaded into the film is approximately 0.5 M, which is a higher concentration than other methods are able to achieve, which means that there are more amine groups present in our film to interact with the copper(II) ions. The only material with a similar loading capacity reported in the literature is the copper(II) adsorption capacity of silica shell microspheres with magnetic cores, a material that is much more expensive and produced via a much more involved synthesis.47

Reusability of the films was also examined, as regeneration of the metal adsorption capacity is highly desirable in heavy metal remediation technology. By the third use of the film, the adsorption capacity of the films had only decreased by 6%. However, it was observed that copper(II) sequestration efficiency of the film reduced nonlinearly, and by the fourth use, adsorption capacity had decreased by 20%, to 8 (±5) mmol/g. Despite the dramatic decrease, this is still a much higher capacity for copper(II) sequestration than most amine-functionalized gels.
CONCLUSIONS

Using kinetic doping, we were able to produce an amine-rich thin film by loading BPEI into silica thin films at an approximately 0.5 M concentration, a 500× increase from the loading solution, without any need for predoping precursor synthetic chemistry or postdoping surface modification reactions. This is a facile, green, and inexpensive procedure.
for introducing amines to silica thin films. To our knowledge, this is the first time BPEI has been doped into silica thin films.

Additionally, these films were preliminarily shown to sequester copper(II) ions at 10 mmol/g, much higher capacity than most technology found in the literature. They also proved to be fairly reusable, with only a 6% decrease in efficacy after three uses, and were stable in solution over the course of a week with less than 1% loss of BPEI from the film. BPEI loaded films are a promising technology that could sequester heavy metal ions from solution, accomplished by more efficient, less expensive, and “greener” practices.

Thin films loaded with BPEI present untapped possibilities for a wide range of applications. This is made possible via kinetic doping to load guest molecules into silica thin films, which has been considered one of the major challenges for more advanced thin-film technology. SEM images suggest that loaded BPEI is distributed throughout the entire 3D silica network inside a film. Due to its ability to sequester copper(II) ions, this presents an intriguing possibility of the construction of transparent and conductive films if the copper(II) can be reduced to metallic copper. Additionally, BPEI in solution has shown antibacterial properties, making BPEI-doped silica thin films a potential platform to develop surface coatings for medical implants to suppress bacterial infection.

## METHODS

### Materials and General Methods.

Tetraethylorthosilicate (TEOS) and 600 and 2500 MW branched polyethyleneimines (BPEIs) were purchased from Sigma-Aldrich. The 600 MW BPEI has a primary/secondary/tertiary amine ratio of 1:2:1, respectively, and the 25,000 MW BPEI has a ratio of 1:1.2:0.76. Phosphoric acid was purchased from EMD Millipore. Premium-grade glass coverslips (25 mm × 25 mm × 170 μm) were purchased from Fisher Scientific. All chemicals and materials were used as received, with the exception of the glass coverslips, which were cleaned prior to use. All UV–vis spectra were obtained via a Shimadzu UV-2101PC UV–vis spectrometer.

### Preparation of Glass Coverslips.

To remove any organic contaminants on the glass coverslip surface, the coverslips were sonicated in an acetone bath for 30 min and rinsed with Millipore water three times to remove all residual acetone. The coverslips were then sonicated in Millipore water for 30 min. The coverslips were then stored in Millipore water until use.

### Preparation of Silica Sol.

Silica sol was prepared by mixing a 1:8:7 molar ratio of TEOS/ethanol/water, respectively, with phosphoric acid acting as a catalyst. A mixture of 55.9 mL of TEOS, 111.8 mL of ethanol, 31.7 mL of deionized water, and 0.62 mL of 1% v/v phosphoric acid at room temperature was prepared for most coatings. The sol was then allowed to age for 20 h undisturbed at room temperature before use.

### Preparation of BPEI-Doped Silica Sol—Gel Thin Films.

Thin films were prepared by drain-coating with a sol solution inside a beaker, based on the drain-coated film preparation method of Crosley et al. After aging for 20 h, the silica sol solution was transferred to a 250 mL beaker, elevated by a jack stand. A clean coverslip was dried with compressed air and immersed in the aged silica sol–gel coating solution while suspended from above. The sol solution was then drained at a rate of 1.36 cm/s; the entire drain coating is completed in less than 2 s. Immediately after the silica sol solution was drained, the jack stand was lowered until the newly coated coverslip was completely exposed to ambient air. The thin film was allowed to age in ambient air for 7.5 min before it was transferred to a loading solution, where BPEI was allowed to load into the film via kinetic doping for 1 week. The loading solution consisted of a 1 mM 25 000 MW BPEI in 10 mM phosphate buffer, adjusted to pH 7.4 with phosphoric acid.

### Quantitative Determination of BPEI Loading.

Detection of copper in the film was done qualitatively with a procedure based on the method for copper detection with BPEI by Wen et al. using the sequestration of copper(II) by BPEI. This produced a dark blue color that could be seen in the film with the naked eye. Quantification of BPEI loading was measured separately, based on the same interaction with copper(II) ions.

The basic amine functional groups in BPEI reacted visibly with the sol–gel film as the film was lowered into the BPEI loading solution, often resulting in a slightly opaque film. The effect is especially prominent around the corner and edges of the films. Due to the degradation in film transparency, the depletion of BPEI from the loading solution was used to quantify the amount of BPEI loaded. Films were removed from the loading solution after 1 week of loading time, and the loading solution was saved for testing. Excess loading solution, stored under the same conditions without exposure to any film, was also saved as a reference for testing.

The concentration of BPEI in the dopant solution, both with and without exposure to thin films, was then determined spectroscopically by complex formation with a known quantity of copper(II); the resulting complex exhibited two peaks, one intense peak in the UV region (276 nm) and one weaker peak in the visible region (638 nm). The UV peak was chosen for the determination of BPEI loading, as the peak at 638 nm was too weak to quantify the small depletion of BPEI in the loading solution. The solutions could be minimally diluted such that the absorbance would fall in the linear range of the peak at 276 nm. The difference in copper(II) concentration for the solutions that had been used to load films and the solution that had not was used to calculate the number of moles of BPEI loaded into the film. A control experiment was performed by placing a clean glass coverslip into the dopant solution for 1 week, and the same difference method was used to show that BPEI was depleted noticeably from the loading solution only in the presence of a silica sol–gel thin film.

### Quantitative Determination of Copper(II) Sequestration and Reusability.

Sequestration of copper(II) ions was also measured based on the method of Wen et al. A concentration curve was made with varying amounts of copper(II) chloride and constant 1 mM BPEI at 638 nm. The peak at 638 nm proved more suitable than the 276 nm peak in this measurement due to the relatively high concentration of copper ions, as it showed linearity in the concentration range being tested. Five identically prepared BPEI loaded films were placed into a solution of 20 mM copper(II) chloride and allowed to equilibrate for 30 min. The five BPEI loaded silica films were then removed from the copper(II) solution, and the concentration of copper(II) remaining in the solution was measured at 638 nm after the addition of 1 mM BPEI. This was compared to the original 20 mM copper(II) chloride solution, and the decrease in copper(II) ion concentration was calculated. An average
mass for the films, obtained from 15 samples, was then used to calculate the amount of copper(II) sequestered per gram of film.

To examine the reusability, the five films that had been tested for copper(II) sequestration were then put into a 10 mM EDTA solution for 30 min. The films were rinsed, dried, and put back into a fresh 20 mM copper(II) chloride solution. The films were again allowed to equilibrate for 30 min; the concentration of copper(II) remaining in the solution was measured again to assess the copper(II) sequestration efficiency of the films. This cycle was repeated until a significant decrease in copper(II) sequestration was observed.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02275.

Concentration curve for 1 mM copper(II) chloride and varying amounts of 25 000 MW BPEI at a wavelength of 276 nm, and an image of the BPEI loaded films at delay times of 7:00–9:00 min, with a drain speed of 1.36 cm/s (PDF).

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

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