Sensing Coatings Developed from Polycarboxylic Acid Hydrogels

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Abstract

The primary objective of the current research is to introduce a new method for obtaining free-standing PMAA hydrogels which can be used as sensing coatings. The preparation was done by layer-by-layer deposition of polymethacrylic acid (PMAA) and poly-N-vinylpyrrolidone (PVPON) on a silicon wafer with thick silicon oxide layer using a spin-coater. PMAA hydrogels were then produced by chemical cross-linking of the H-bonded PMAA/PVPON film by using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and ethylenediamine (EDA) with further release of PVPON at phosphate buffer with pH = 8. The minimum thickness for the method and the influence of gold nanorods on mechanical stability of hydrogels was explored during the research. Finally, hydrogels were characterized using ellipsometry, atomic force microscopy and transmission electron microscopy.

Multilayer construction and cross-linking

Multilayer construction: PMAA and PVPON solutions were used to perform the layer by layer coatings to obtain H-bonded PMAA/PVPON films (Figure1). Briefly, the polymer solutions were deposited at pH = 2.5 with 1 mg/mL concentration of solution using spin coater at rotational speed 3000 rpm for 30 s; then rinsed twice with the buffer solution to get rid of unattached polymer.

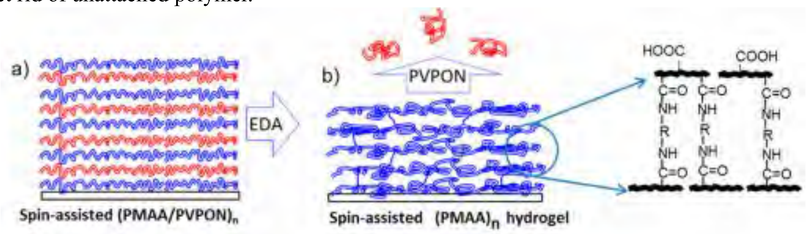

Figure 1. LbL assembly approach for the construction of thin multilayer hydrogels.

Crosslinking : H-bonded PMAA/PVPON films were chemically crosslinked using EDC and EDA system. Quickly, the films were poured into the EDC solution with concentration 5 mg mL-1 at pH = 5.0 for 40 minutes, then crosslinked with EDA solution using 0.012 mg mL-1, and 0.01 M of phosphate buffer at pH = 5.8 for 16 hours. The minimum swelling is observed at pH 4.86 due to ionic interactions between negatively charged carboxylic groups of ionized PMAA and charged primary amino groups remaining after crosslinking. The increase in swelling at pH values below and above 5 is cause by excess of positive or negative charges (figure 2).

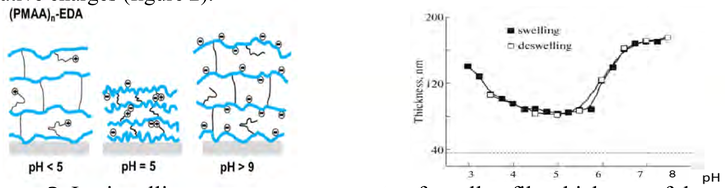

Figure 2. In situ ellipsometry measurements of swollen film thickness of the crosslinked hydrated (PMAA)10 film as a function of pH supported by 0.01 M phosphate buffer.

Release of hydrogels

The crosslinked hydrogels were used for release by using HF/NH4F etching buffer solution at pH = 5. Briefly, wafers with thick silicon oxide layer with attached hydrogels on them were submerged into etching buffer solution. Then the buffer solution dissolves SiO2 layer, so that free-floating hydrogels can be obtain as shown in figure 3. From that point onward, HF solution was replaced with DI water of pH = 5 and then the hydrogels were collected onto silicon wafers for future characterizations.

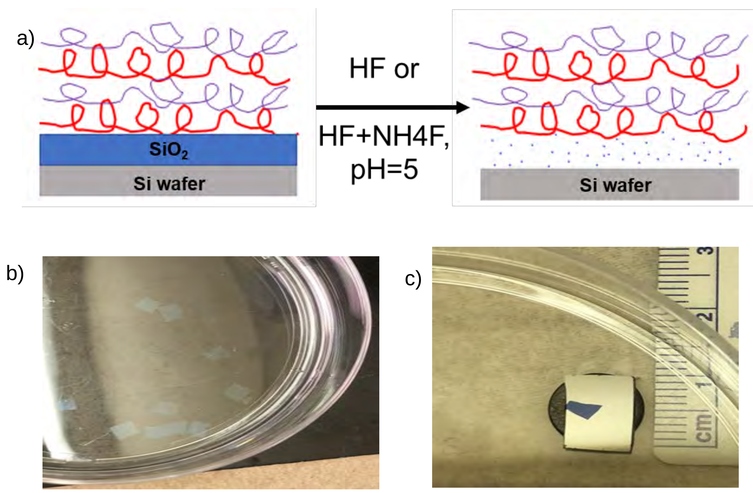

Figure 3. (a) Schematic of obtaining free-standing hydrogels, (b) free-floating films in DI solution at pH=5, and (c) hydrogel transferred onto Si wafer surface and dried.

AFM analysis of PMAA hydrogels

The hydrogels were characterized by AFM analysis before and after the release to check for surface morphology of the hydrogels. After the release, roughness remain the same what means the release does not effect on roughness.

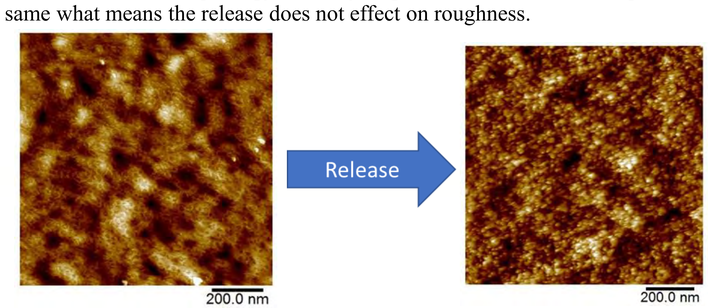

Figure 5. AFM images of PMAA before (left) and after (right) the release

Incorporation of Gold Nanorods

To incorporate inorganic catalyst within multilayers, PMAA hydrogels were soaked in Au gold nanorods solution in a falcon tube secured with foil and left in a dark area over night. Due to diffusion, Au nanorods go inside the swollen hydrogels and when it shrinks, the Au nanorods are trapped inside. Gold nanorod-containing LbL hydrogels were characterized on TEM analysis as shown in figure 6.

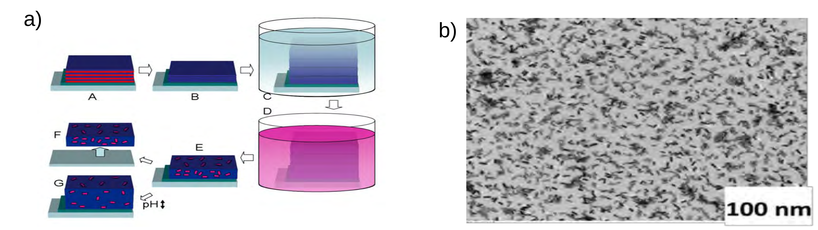

Figure 6. (a) LbL hydrogels containing gold nanorods in pH sensitivity and (b) Afm and Tem analysis of PMAA with gold nanorods

Conclusion

Based on our results, the new method for obtaining free-standing films and hydrogels was accomplished. The multilayer was isolated from the substrate through dissolving substrates with no damage on the multilayer. We were able to establish the lower threshold of thickness for this method and obtain hydrogels with smooth surface and incorporated inorganic catalysts such as gold nanorods within their structure.

References

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