A Study of Inorganic-Polymer Hybrid Films for Various Surface Functionalization

Byoung-Soo Park, Zhou Lui, Hye-Seung Jin and Sung Yun Yang*

Department of Polymer Science and Engineering, Chungnam National University, 220 Gund-Dong, Yuseong-Gu, Daejeon , South Korea

ABSTRACT

We have studied polyelectrolyte multilayer(PEM)[1] coatings on flat and colloidal particles. Layer-by-layer deposition enables to create conformal coatings with polyelectrolytes, which are water-soluble polymer, with various kinds of water-dispersed materials such as magnetic or gold nanoparticles. Especially the multilayers formed by using weak polyelectrolytes or polymers with hydrogen-bonding capacity exhibited interesting stimuli-responsive behaviors in addition to chemical functionalities.[2-4]

Here we demonstrate new approaches to use this layer-by-layer technique for non-conventional materials like polyelectrolytes. We used gold nanoparticle and cyclodextrin for these experiments and they both were modified by adding a chargeable group. This modification made them able to form multilayer coatings on the substrates. Modified cyclodextrin(CyD) moieties were applied on colloidal particles as well as flat substrates. These coatings were examined by zeta-potential analysis and fluorescence microscope. Additionally, biological interactions on the PEM coatings using epithelial and neuronal cells show an excellent improved biocompatibility. These coatings will provide a great possibility of introducing chemical and biological functionalities to the surfaces of interests.

INTRODUCTION

The naturally occurring cyclodextrins were the first receptor molecules whose binding properties toward organic molecules were recognized and extensively studied.[1] Molecular receptors are defined as organic structures held by covalent bonds that are able to bind selectively, without forming covalent bonds, ionic or molecular structures by means of various intermolecular interactions. Intensive studies of cyclodextrins have been carried out in solution state, but not much done in creating cyclodextrin films. Especially combining cyclodextrin molecules with ionic material, such as magnetic particle, would give a new opportunity to study multi-functional material.

We created polyelectrolyte multilayers (PEMs) on flat and colloidal particles using hydrogen bonding or electrostatic interactions [2-5]. This process is very powerful tool to create various functional coatings. We here used the technique to create multilayer films containing cyclodextrins which are immobilized in polymer film on magnetic particles. We synthesized a new cyclodextrin that has ionizable units and assembled it with oppositely charged polymer by layer-by-layer process. The resulting CyD-containing multilayer films show exhibited excellent

NSTI-Nanotech 2010, www.nsti.org, ISBN 978-1-4398-3415-2 Vol. 3, 2010

biocompatibility. The PEM coatings including CyD on magnetic particles were examined by zeta-potential analysis and fluorescence microscope.

Gold nanofilm has received a great interst recently due to its unique optical property, surface Plasmon resonance (SPR). SPR absorbance results in a visible color of the metal nanoparticle. SPR reflectivity changes upon the event of the molecule adsorption onto the metal surface and the change is very sensitive with even a small amount of absorbates. This phenomenon can be used to detect the binding of the biomolecules. Therefore, we used AuNP to form a coating on a biochip by layer-by-layer deposition.

These PEM-coated magnetic particles provided the versatility on introducing chemical and biological functionalities using reactive groups of the PEM films. These new polymer films have a great potential in biological applications including tissue engineering and biosensor.

EXPERIMENT

Materials. Poly(allylamine hydrochloride) (PAH), poly(acrylic acid) (PAA) and polyacrylamide (PAAm) were purchased from Polysciences. Modified cyclodextrin, P(β-CyD), was synthesized by using epichlorohydrin(EP) and choline chloride(CC) to convert hydroxy group of on β-CyD into amine groups. β-CyD, EP and CC were purchased from Aldrich. AuNP particles were synthesized and surface functionalized by the method that previously reported.[6] The polyelectrolyte solutions were prepared with a concentration of 0.001 M (based on monomer units). De-ionized water(~18 MΩ cm) was adjusted to pH 3.0 in all aqueous solutions and rinsing. Carboxylated paramagnetic polystyrene particles (PS-COOH) between 1 micron and 2 micron in size (2.65% aqueous solution) were purchased from Polysicences. Ferromagnetic iron oxide particles were synthesized.

Multilayer formation. The dipping solutions of PAH, PAA and PAAm were pH-adjusted with 0.1M NaOH or HCl aq. solution. PAA and PAAm solutions were pH-adjusted to pH 3.0/3.0. In the case of AuNP deposition with PAH was done at the pH condition of 8.5 for both materials. The multilayer film was prepared by a repeated, sequential dipping of the two polymer or AuNP solutions separated by rinsing steps.

The multilayer film was prepared by a repeated, sequential dipping of the two polymer solutions separated by rinsing steps. 100μL of the aqueous PS-COOH (2.65w% solids) with 900μL deionized water dispersion in a micro tube was centrifuged, and the supernatant was removed. After rinsing once with deionized water, the PS-COOH particles in the micro tube were redispersed in 1mL of PAH at pH 6.0 adsorption solution, and then by immediate vortexing and sonication (less than 30 s). The dispersions after which the PAH was allowed to adsorb were then centrifuged, the supernatant was replaced by water to rinse. The PAH layer-deposited particles was redispersed to the PAA solution, vortexing, centrifuged, removed, rinsed in water. These steps were repeated to build multilayer films.

Cell Culture. 293 epithelial cells were incubated in serum-containing medium under 5% CO_2 at 37^oC and provided with a fresh media in three days.

Characterization. Contact angle measurements were performed with de-ionized water droplets by contact angle analyzer. The ζ-potentials of coated particles were determined with a Zeta-Potential & Particle instrument by taking the average of five successive measurements.

Fluorescence microscopy images and cell images were taken by Olympus inversed phase optical microscope.

RESULTS AND DISCUSSION

We prepared the polyelectrolyte multilayer film which was comprised of PAA, PAAm and CyD polymer. The magnetic colloidal particles coated with fluorescent-dye-labeled PAA/PAAm multilayers are uniformly coated with the H-bonded multilayers.

Zeta-potential as a function of polyelectrolyte layer number for PAA/P(CyD) coated at 3.0/3.0 is presented in Figure 1. The alternating values in both cases, PAH/PAA with P(CyD) and PAAm/PAA with P(CyD), demonstrate a successful recharging of the particle surface with each polyelectrolyte depositon.

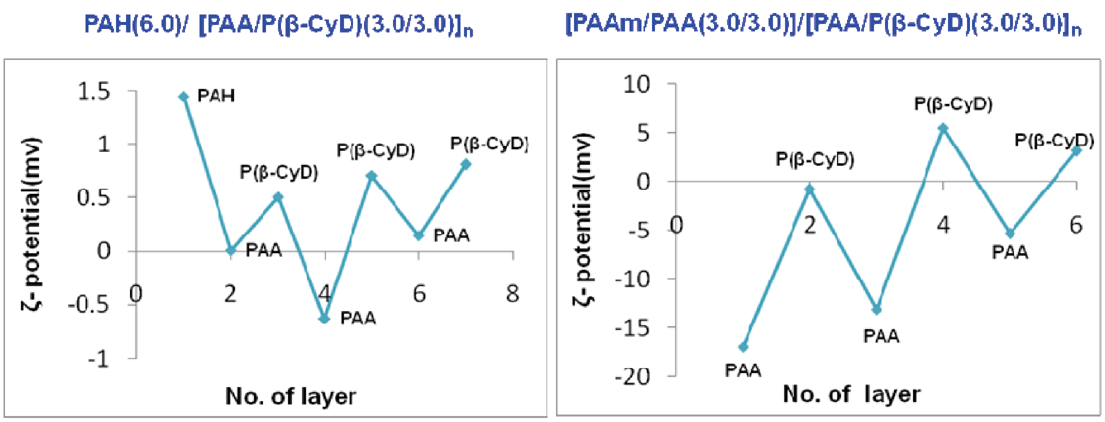

Figure 1. Zeta-potential values for each deposition step of the multilayer coating on colloidal particles.

We also studied cellular interactions with these polyelectrolyte multilayer films added CyDs. As dipping in the CyD solution, surface of the film changed to a good adhesive surface for cell-adhesion (Figure 2). Further studies including host-guest complexation using cyclodextrin cavity is also undergoing.

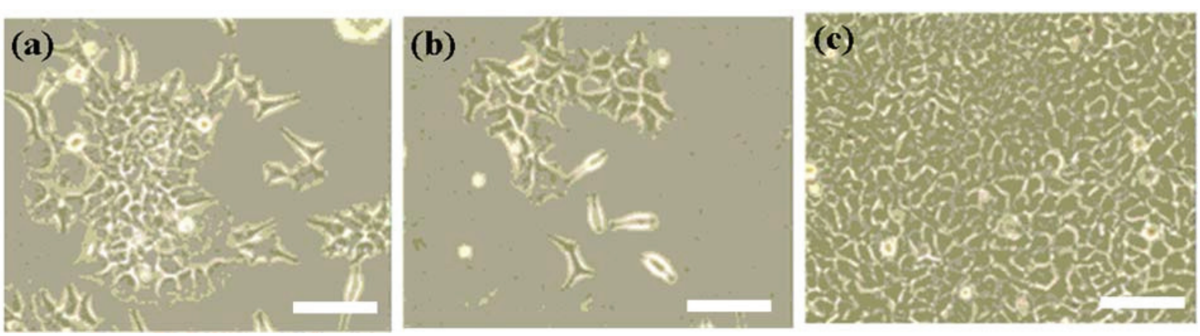

Figure 2. Microscopic images of the cellular interactions on the multilayer coatings. (a) PAH, (b) PAA and (c)P(CyD) top surfaces. (scale bar, 200 μm)

Carboxylate-modified gold nanoparticles(AuNP) were successfully deposited on a chip (either silicon or gold chip designed for biochip application) with PAH using electrostatic interaction. Figure 3 shows the SPR absorbance changes of the deposited films, which proves a smooth growth of the film as increasing the number of deposition.

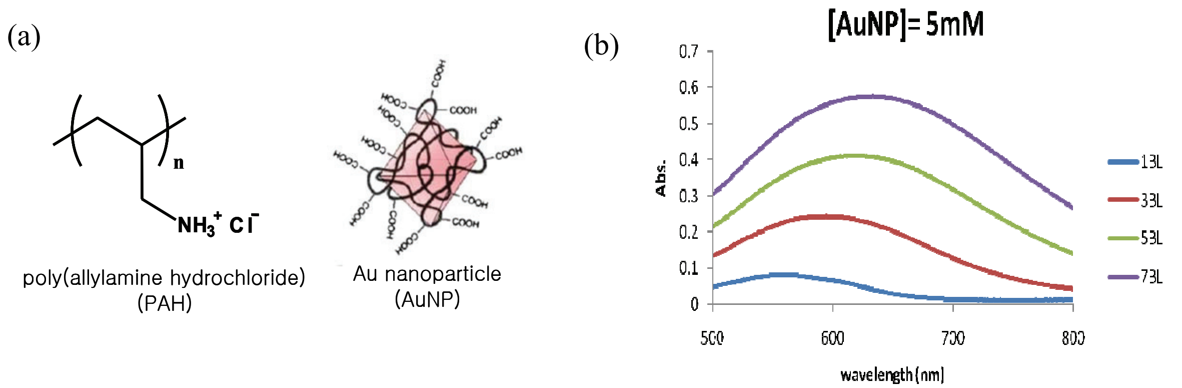

Figure 3. The chemical structures of PAH and surface-functionalized AuNP (a) and UV spectra of the AuNP/PAH multilayer films assembled at pH(8.5/8.5) (b).

CONCLUSIONS

We prepared β– cyclodextrin (CyD) containing polyelectrolyte multilayer films onto magnetic colloidal particles, which were prepared at various pH assembly conditions, and studied the surface and optical properties of the films. Complexation behaviors of these CyD containing multilayer films were examined by short dipping of the deposited films in solutions of several aromatic compounds. We also tested cellular interactions on these multilayer films. This paper will give insights for studying supra-molecular systems in pseudo-solid state.

We also studied cellular interactions with these polelectrolyte multilayer films using epithelial cells. For example, β-CyD containing multilayer films exhibited excellent biocompatibility. Cells were growing well on these multilayer films. These new polymer films have a great potential in biological applications including tissue engineering.

References

[1] S. Y. Yang et al., *J. Am. Chem. Soc.*, ***119***, 12404 **(**1997)
[2] G. Decher, J. D. Hong, *Makromol. Chem. Macromol. Symp*. 16, 321 (1991)
[3] S. Y. Yang, D. Lee, R. E. Cohen, M. F. Rubner, *Langmuir*, 20, 5978 (2004)
[4] S. Y. Yang, D.-Y. Kim, S.- M. Jeong, J.- W. Park, *Macromol. Rapid Comm.* **29**, 729 (2008)
[5] H.-J. Heong, W.-H. Pyunn, S.Y. Yang, *Macromol. Rapid Comm.* **30**, 1109 (2009)
[6] D. Seo, H. J, Song**,** *Chem.. Commun*, 1276 (2009)

Acknowledgement

This research was financially supported by the Ministry of Education, Science and Technology (MEST) through Korea Science and Engineering Foundation (KOSEF) grant (R01-2007-000-11930-0, R11-2007-050-03003-0).