

## 論文の内容の要旨

論文題目     Ultrathin Membranes of Artificial Lignin  
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### **[1] Introduction**

Lignin, as one of the most abundant nature polymers, accounts for approximately 30% of the organic carbon on earth and exists in almost all terrestrial plants. Chemically, lignin is an amorphous three-dimensionally crosslinked polyphenolic polymer, whose rigid aromatic skeleton carries a large amount of phenolic hydroxyl groups. Because of such aromatic network, lignin is both mechanically tough and chemically resistant to degradation. Recently, many attractive properties of lignin such as antioxidation, UV-shielding, antimicrobial, and antiviral activities were reported and encouraged many researchers to explore lignin-based functional materials for valuable applications. However, one of the serious problems for this direction is the poor processability of lignin. Currently, lignin can be obtained only in a form of a powder and cannot be processed to any other forms without making a composite with other processable polymers, where most of the attractive feature of lignin (mechanical and chemical robustness) would be gone. This fact is a huge drawback for the development of materials based on lignin.

The main topic of my PhD thesis is how I successfully utilized a new method of generating pH gradient on an electrode surface for synthesizing the first example of ultrathin membranes of artificial lignin. Moreover, I demonstrated its application for a separation membrane. In addition, at the early stage of the investigation of ultrathin membrane synthesis, I found an anomalously slow hydration kinetics of a self-assembled monolayer on hydrophobic surfaces in water. This finding provides a new fundamental molecular insight about how protein-ligand and protein-protein interactions take place.

### **[2] Fabrication and Characterization of Ultrathin Membranes of Artificial Lignin**

Ultrathin membranes bearing both nanometer thickness and macroscopic size, have garnered intense scientific interest because of their potential applications in selective transport,

flexible electrical skin and electrochemical devices. Two important structural features are requested for these applications to have, one is mechanical/chemical robustness, and the other is homogeneous structure without defect over a large area. It is still a big challenge to achieve these specific targets in the development of ultrathin membranes. Lignin, as a high mechanically/chemically robust polymer would be an ideal candidate material for ultrathin membrane materials, but never fabricated to a membrane due to its low processability. Here, the author developed an extremely simple technology to fabricate a lignin-mimetic ultrathin membrane with an aspect ratio of size and thickness greater than  $5 \times 10^5$ .

The ultrathin polyphenolic lignin-like membrane was synthesized on the surface of a silicon wafer as working electrode in a homemade cell. An aqueous solution containing resorcinol (0.5 M) and formaldehyde (1.0 M) was added into the reaction chamber. After applying +5.0 V (vs. Ag/AgCl) to the device for 1 min using a potentiostat at room temperature, these two monomers undergo polymerization on the electrode surface. In contrast, without formaldehyde, the membrane was not observed under otherwise identical conditions. Considering that the positive potential can generate a pH gradient of a  $\text{OH}^-$ , the membrane formation is highly likely due to the addition condensation reaction between resorcinol and formaldehyde just like the formation of phenol resin. Interestingly, when the electrode was immersed into water, the ultrathin membrane formed on the electrode surface spontaneously floated on water.

The chemical structure of the ultrathin membrane was confirmed by Fourier transform infrared spectrometry (FT-IR) and pyrolysis–gas chromatography–mass spectrometry (Pyr-GC/MS). The thickness and the surface roughness of the membrane was determined to be  $57.7 \pm 0.46$  nm and 2.20 nm, respectively, by using atomic force microscopy (AFM). Nanoindentation measurement confirmed that the Young's modulus of the nanomembrane is 16.8 GPa. This value is one order of magnitude higher than conventional polymeric ultrathin membranes. Such mechanical robustness is likely derived from the three-dimensionally cross-linked aromatic skeleton of nanomembrane. In order to investigate chemical stability, the membrane were soaked into 0.5 M HCl and 0.5 M NaOH solution for one month. Surprisingly, AFM observation revealed that the thickness and surface morphology showed negligible change, demonstrating its excellent chemical robustness. The observed mechanical and chemical robustness is appropriate for the membranes to be utilized under strict engineering environments, such as high pressure, strong basic or acidic conditions.

Our novel electrochemical technology can tailor membrane thickness down to several nanometer increments by changing the synthetic conditions. The thickness of membrane increased from 30 to 75 nm with reaction time, and reached a plateau at 2 min. This is likely due to the decreased diffusion rate of the monomers to the electrode surface once the membrane became thick enough. When the reaction voltage was reduced to +2 V, the reaction

speed became lower so that it took 10 min to reach the same thickness of a membrane obtained from that using +3 V or higher. This is probably due to the weakened pH gradient formed on an electrode surface with lowered potential. Other phenolic derivatives with formaldehyde can also be used to synthesize such artificial lignin polyphenolic membranes with thickness below 100 nm.

### **[3] Ultrafast Water Purification Behavior of Artificial Lignin Membrane**

Purification and separation using membranes are known to be an energy-efficient process and often employed in industry. Such membranes are requested to meet two requirements; one is to be robust under strict engineering environments, and the other is to have permeability for high process efficiency. Regarding the permeability, reducing the membrane thickness is the straightforward way to achieve high value, especially to a thickness below 100 nm. The ultrathin artificial lignin membrane, described in Chapter 2, was discovered to have high mechanical and chemical robustness. Considering the thickness of 58 nm, the membrane is also expected to have high permeability. In Chapter 3, water permeability and purification capability of the ultrathin artificial lignin membrane was investigated.

The artificial lignin membrane was first placed onto a porous polymeric supporting membrane (pore size = ~100 nm) and prepared a thin film composite (TFC). The water permeation was investigated using the TFC membrane by a homemade dead-end filtration apparatus. Water has shown a high water permeability of  $21.98 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ . This value is one order of magnitude higher than typical polyamide membrane used for water desalination. The separation performance of artificial lignin TFC membrane was also evaluated by using an aqueous solutions of various dyes. To our surprise, brilliant blue G ( $M_w = 854.02 \text{ g mol}^{-1}$ ) could be completely separated (rejection ratio = 99.9%) while maintaining high permeability ( $21.76 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ). Furthermore, the separation performance of artificial lignin membrane was highly dependent on the charge of the dye molecule rather than the size, which is very different compared to reported examples. As for the smaller molecules ( $< 350 \text{ g mol}^{-1}$ ), positively charged ones had higher rejection rate than negative ones. For example, the rejection rate of methylene blue ( $M_w = 319.9 \text{ g mol}^{-1}$ , charge = +1) and methyl orange ( $M_w = 327.3 \text{ g mol}^{-1}$ , charge = -1), whose molecular weight were similar but the charge were opposite, were 96.8% and 45.7%, respectively. We supposed that partial deprotonation of the phenolic hydroxy group on the polymeric skeleton of the membrane endowed the negatively charged feature, and thus positively charged dyes can be trapped by electrostatic attractive force.

### **[4] Anomalously Slow Hydration Kinetics of Self-Assembled Monolayer at Hydrophobic Interface**

The hydration behaviors of polar molecules at a hydrophobic surface are long-standing interest in protein and cellular interactions. Several theoretical proposals have been made to elucidate peculiar properties of water on hydrophobic surfaces. However, before our recent work, this issue remained unexplored, mainly because analytical methods such as second harmonic generation (SFG) and AFM, mostly employed for investigating interfacial events, are not informative enough to render the behaviors of complex functional groups on the surface. In Chapter 3, I fabricated self-assembled monolayers (SAMs) composed of polar tetraethylene glycol chains appended with nonionic (Fmoc) and ionic (FITC) fluorescent head groups on silicon wafer covered by space-filling C<sub>2</sub> alkyl chains (SAM<sub>C<sub>2</sub></sub>) as a model and investigated their hydration events.

In the dry state, both Fmoc-SAM<sub>C<sub>2</sub></sub> and FITC-SAM<sub>C<sub>2</sub></sub> were essentially non-fluorescent because their head groups were adjacent to the substrate surface and thus photo-chemically quenched by distance-dependent energy transfer. In deionized water, whether their head groups are nonionic or ionic, the hydration event occurs slowly and requires  $\geq 8$  hours to reach a thermodynamic equilibrium at ambient temperatures. This process was also monitored by in situ ellipsometry and both Fmoc-SAM<sub>C<sub>2</sub></sub> and FITC-SAM<sub>C<sub>2</sub></sub> became gradually thicker with time and eventually reached a constant thickness in 8 h. Concerning that a contact angle of a water droplet on a hydrophobic surface reaches a constant value in seconds upon equilibration, the observed hydration kinetics are surprisingly slow. This anomalous hydration behavior is likely due to a peculiar hydrogen-bonding network known to form on hydrophobic surfaces. These results may certainly contribute to the deeper understanding of how polar functional groups on protein surfaces are hydrated and dehydrated and interact with different guest molecules.

## **[5] Conclusion**

In the PhD thesis, I developed a novel and universal method to fabricate an ultrathin defect-free freestanding artificial lignin membranes, which is mechanically and chemically robust, in a very simple manner. The key technology used here is the pH gradient generated on an electrode surface which leads the monomers to polymerize only at the interface of the electrode. Furthermore, the composite membrane comprising artificial lignin membrane and porous supporter exhibited ultrafast water permeability, and excellent selectivity for nanofiltration applications. Considering many interesting properties of natural lignin, such as antimicrobial activity and antioxidation property, these ultrathin artificial lignin membranes might be applicable in life science. Besides, the anomalously slow hydration phenomenon at hydrophobic interface gave a clue to understand how such a hydrogen-bonded water network dominates biological functions of proteins.