

Title	溶液を用いた分子層堆積(MLD)法によるポルフィリン含有ポリ尿素薄膜の作成
Author(s)	Uddin, S. M. Nizam
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Description	Supervisor:長尾 祐樹, マテリアルサイエンス研究科, 博士

# Dissertation Abstract

Synthesis of organic thin film materials on solid surfaces is important for prospective applications in many research fields today. One of the simple and versatile techniques to prepare nanometer scale multilayer thin films is solution based molecular layer deposition (MLD). Organic thin film growth depends on several factors such as solid surface properties, self-assembled monolayer, as well as optimized reaction condition.

First part of this research was focused on the study of aminosilane self-assembled monolayer formation on Si/SiO<sub>2</sub> surfaces. A major problem of aminosilane-modified surface is their chemical stability. To examine the issue of losing surface functionality, I prepared the self-assembled monolayer of one and three alkoxy group containing 3-aminopropyldimethyl ethoxysilane (APDMES) and 3-aminopropyl trimethoxysilane (APTMS) on SiO<sub>2</sub> substrates respectively. Silanization condition of APDMES was investigated in four different solvents under various reaction conditions. APDMES layer prepared at both RT and high temperature (70 °C) in toluene for 3 hr shows the highest N-at. % along with highest free amine %. In contrast, APTMS-modified SiO<sub>2</sub> substrate was prepared in ethanol at RT for 1, 2, 3hr of silanization and found that 1 hr silanization is enough for APTMS-modification on SiO<sub>2</sub>. The chemical stability of APDMES and APTMS-modified SiO<sub>2</sub> substrates were also investigated after 7 hr immersion into H<sub>2</sub>O and 0.1 M HClO<sub>4</sub> solution at 40 °C and RT respectively. Contact angle and XPS analysis showed that 22.4 % APDMES and 6.7 % APTMS were removed from the surface when the modified substrates were immersed into H<sub>2</sub>O at 40 °C for 7 hr. On the other hand, 38.7 % APDMES and 14.9 % APTMS were removed from the surface when the modified substrates were immersed into 0.1 M HClO<sub>4</sub> (aq) solution at RT for 7 hr. Thus Indicating, three alkoxy groups containing APTMS is more chemically stable (in hot H<sub>2</sub>O and HClO<sub>4</sub>) than one alkoxy group containing APDMES.

In the second part of this article, I demonstrated a solution-based molecular layer deposition (MLD) approach to prepare porphyrin-based covalent molecular networks on APTMS modified substrate surface using the urea coupling reaction between 1,4-phenylene diisocyanate (1,4-PDI) and 5,10,15,20-tetrakis-(4-aminophenyl)porphyrin (H<sub>2</sub>TAPP) at room temperature. Multilayer growth was investigated under different relative humidity (RH) conditions. Sequential molecular growth at low relative humidity (≤10% RH) was observed using UV-vis absorption spectroscopy and atomic force microscopy (AFM). The high-RH condition shows limited film growth. Infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS) revealed the polyurea bond formation in sequential multilayer thin films, demonstrating that stepwise multilayer film growth was achieved using the urea coupling reaction.

**Keywords:** Self-assembled monolayer, Molecular layer deposition, Porphyrin, Polyurea, Covalent linkage, Thin film.