Size-sensitive protein adsorption on silicon surfaces grafted with poly (*N*-isopropylacrylamide)

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Introduction: Poly(*N*-isopropylacrylamide) (PNIPAAm) is a well known temperature-sensitive polymer exhibiting the volume phase transition near the "lower critical solution temperature" (LCST) at 32°C. When it is immobilized onto a flat substrate, the LCST behavior leads to temperature-responsive property, such as wettability, cell adhesion, and biocompatibility, etc., changes on the surface [1, 2]. For applications in controlled drug delivery, separation science, and other biological engineering, the surfaces which can adsorb proteins in one condition and resist them in another condition is of crucial importance. So it is interesting to evaluate protein adsorption onto PNIPAAm grafted surface as temperature changes around the LCST. Especially, for protein purification and separation applications, it is essential to investigate whether different proteins show different temperature-responsive adsorption behaviors. In this report, PNIPAAm grafted silicon surfaces were prepared via surface-initiated atom transfer radical polymerization (SI-ATRP) and the adsorption of three model proteins, Human serum albumin (HSA), fibrinogen, and lysozyme with different sizes and charges were examined. The results indicate that the PNIPAAm modified surface exhibits a size-sensitive protein adsorption property.

Methods: The pretreatment of silicon wafers and SI-ATRP of NIPAAm was carried out following the procedures in a previous report [3]. The surface wettability change with temperature was investigated by water contact angle. The adsorption of three proteins in phosphate-buffered saline (PBS) (pH 7.4) at different temperature was evaluated using a radiolabeling method.

Results: SI-ATRP of NIPAAm was conducted by immersing the initiator-modified silicon wafers into a reaction mixture at room temperature. Homogeneous and dense PNIPAAm layer were prepared successfully with a thickness of ~38.1nm. The static contact angle measured at 23°C (~58.2°) and 37°C (~79.8°) indicated the thermo-responsive wettability of the modified surface, , as illustrated in Figure 1. This phenomenon could be elucidated by the competition between intermolecular and intramolecular hydrogen bonding during the phase transition [4].

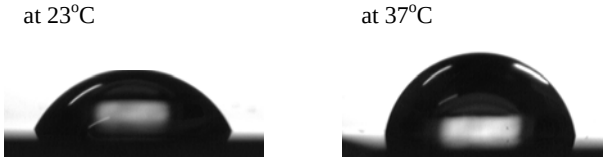

Figure 1. Contact angle images for Si-PNIPAAm surface under different temperatures.

The adsorption of three proteins on Si-PNIPAAm surface measured at room temperature (23°C) and the corresponding increased adsorption ratio (from 23°C to 37°C) were shown in Figure 2. At room temperature, the smallest protein lysozyme exhibites the largest adsorption; while as the temperature rising, its increased adsorption extent was the lowest. This protein size dependant adsorption behavior may be interpreted by Halperin's model and Norde's model, in which proteins with different size would adopt their respective modes of protein adsorption and were adsorbed on different positions of PNIPAAm brushes [5, 6].

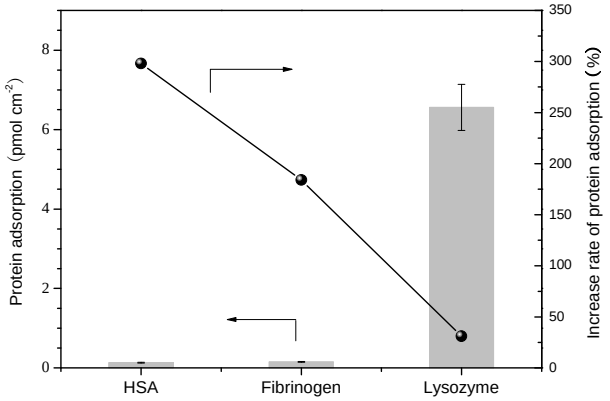

Figure 2. HSA, fibrinogen and lysozyme adsorption at 23°C and the increase rate of their adsorption (from 23°C to 37°C) under PBS buffer on Si-PNIPAAm surfaces

Conclusions: In this work, PNIPAAm modified silicon surfaces were prepared by SI-ATRP. The surfaces exhibited thermal-responsive wettability and a certain extent size-sensitive protein adsorption property, which is beneficial to potential applications such as protein purification and biosensors.

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