

Studies of the Synthesis and Assembly of Polymers at Gold Surfaces

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Abstract

The formation of polymer films and brushes at surfaces is an essential step in the fabrication of devices interfacing with biological systems, such as biosensors, drug delivery systems, medical implants and tissue engineering scaffolds. The aim of this project was the fabrication of patterned polymers on the surfaces of gold substrates. Two different fabrication techniques were investigated based on the grafting-from and grafting-to approaches.

For the grafting-from method, dithiocarbamate-based initiators were attached to gold via a disulfide functionality. The initiators were synthesised from hydroxyl-terminated disulfides and alkyl/aryl chlorides, which were subsequently reacted with diethyldithiocarbamates salts. Materials synthesised in this research were purified and characterised using column chromatography, elemental analysis, nuclear magnetic resonance, infrared spectroscopy and mass spectrometry. Polymer (polyacrylamide) was grown from the grafted initiator surfaces on gold via living radical polymerisation, by activating the initiator with ultraviolet irradiation. Techniques such as photolithography (using masks) and microcontact printing were used to pattern these surfaces.

For the grafting-to method, thiol ended polymers were synthesised in solution prior to deposition on the gold surface. Polymers were first synthesised using benzyl diethyldithiocarbamate iniferters or chain transfer agent, thioacetic acid combined with standard radical initiators. The polymers were purified by dialysis. The terminals were hydrolysed to produce free thiol groups using sodium hydroxide. Hydrolysis was followed by ultraviolet/visible spectroscopy. Gel filtration chromatography was used to desalt the polymers, which were then freeze-dried. The molecular weight of the polymers was determined by gel permeation chromatography before they were self-assembled onto gold. Patterns were achieved via photooxidation lithography through masks with an ultraviolet laser.

Polymer surfaces were characterised throughout the research by wettability studies, fluorescence microscopy, surface plasmon resonance and atomic force microscopy.

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