Modification of Carbon-Based Materials with MPC Polymer Brush for Applications in Intracellular Nanosensors

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Introduction: Detection of local concentration of ions, metabolite and drugs in living cells is important for drug development in pharmaceutical companies. Recently, carbon-based electrochemical nanosensors have been developed, which enables such measurements. However, protein adsorption onto the carbon electrode surface results in lower sensitivity of the sensors. In this study, carbon-based materials were modified with poly(2-methacyrloyloxyethyl phosphorylcholine) (PMPC) brushes, which have been shown to suppress protein adsorption [1], through surface-initiated atom transfer radical polymerization (SI-ATRP).

Methods: Cyclic olefin polymer (COP) surfaces were used to characterize the surface properties of the polymer brushes. First, the surface initiator, perfluoroaryl azide-2-isobromobutyrate (1wt% in methanol), was immobilized on COP by UV (254 nm) photolysis reaction for 5 min [2]. Then, 50-unit MPC polymer brushes were grown on the surface initiator through SI-ATRP by immersing the substrate in methanol containing MPC monomer (0.5 M), CuBr (0.01M), 2,2'-bipyridyl (bpy) (0.02M) and ethyl-2-bromoisobutyrate (0.01M) at 20°C for 20 hrs. Polymer brushes of different unit lengths (20~150 units) were also synthesized. MPC-modified surfaces were characterized by brush thickness, graft chain density, wettability and elemental composition. Also, glassy carbon electrodes (GCE) were modified by the same procedure to evaluate the electrochemical properties of the MPC polymer brushes. Specifically, PMPC-modified GCE was used to measure the electron transfer rate of a potassium ferrocyanide solution (10mM, aqueous) through cyclic voltammetry (CV), using AgCl/Ag reference and Pt auxiliary electrodes.

Results: Surface properties were evaluated for initiator- and PMPC-grafted COP substrates. The presence of the surface initiator and MPC polymer brush were confirmed from the result of the atomic composition analysis by XPS (e.g., N and P peaks). The thickness of MPC polymer brushes was also evaluated by ellipsometry and found to be roughly 4~10 nm depending on the polymer chain lengths. And the result of contact angle measurements showed the conversion of hydrophobic COP surfaces (95° water in air) into hydrophilic MPC-modified surfaces (10°). Also, electrochemical properties were evaluated for initiator- and PMPC-grafted GCE by CV. Clear changes in the cyclic voltammogram were observed when the initiator was grafted, where the shift peaks of oxidation and reduction suggested a slower electron transfer rate. However, when further grafting of MPC polymer brush by ATRP was performed, there was no further change. It was suggested that the PMPC brushes themselves were not a hindrance to the electrochemical measurements. Overall, the results show successful modification of the carbon-based surfaces that may be applied to the nanosensors for the detection of the localized intracellular drug concentrations.