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Electrochemically Induced Deposition of Thiol-Based Monolayers onto Closely Spaced Microelectrodes

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We report on an electrochemical protocol for the selective formation of self-assembled alkanethiol monolayers on a given microelectrode in the presence of a nearby second one. The procedure relies on the accelerated self-assembly of alkanethiols in ethanolic solutions under a *cathodic* polarization. Voltammetric "blocking" and electrochemical quartz crystal microbalance experiments, along with optical surface imaging, are used for demonstrating the selective electrochemisorption process. Using closely spaced electrodes (with 6 μm gaps), we demonstrate that only electrodes kept at negative potentials have been coated. Such attractive behavior is attributed to the simultaneous cathodic removal of an inhibitory surface layer. The high spatial resolution opens the way for localizing different reactive chemistries onto predetermined locations of sensor arrays.