Chapter - 5

SELF ASSEMBLED MONOLAYERS
Figure 1. Langmuir Blodgett methodology. a) Surfactant in water. The black dot represents the head and the line represents the tail. The molecules are disordered. b) Partially compressed monolayer by the pushing of a barrier across the film surface, c) ordered monolayer by the application of pressure, d) immersion of the substrate in an ordered film, e) transfer of the monolayer onto the substrate and f) densely packed monolayer on the substrate.
Figure 2. Schematic showing the basic structure of 2D SAMs.
Figure 3. Schematic structure of a monolayer of alkanethiol on Au(111). In (a) a layer of hexagonally arranged gold atoms is shown (dotted hexagon). Each corner of this dotted hexagon corresponds to the center of the gold atom. On top of this surface the alkanethiol molecule chemisorbs. The structure of the sulphur atoms is also hexagonal (solid hexagon), as indicated. These atoms sit on three-fold sites created by the gold atoms. In (b) an assembly of thiolate chain is shown, this will form a two dimensional sheet on the surface. In (c) an extended chain is shown, it shows a zig-zag assembly. The tilt angle is shown. It is also shown that the chains have rotational freedom.
Figure 5. Nine molecule section of full coverage C_{16}H_{33}SH monolayer on Au(111) based on molecular mechanics energy minimization calculation showing the tilted chains. (A. Ulman Chem. Rev. 96 (1996) 1533).
Figure 6. Overlayer structure of thiol on Ag(111). The open circle represents the silver atoms. The grey and black circles represent the sulphur at the hollow site and on-top site, respectively. (A. Ulman, Chem. Rev. 96 (1996) 1533).
Figure 7. Orientation of alkyl chains on AgO and Al₂O₃ surfaces. In the case of AgO the chains are tilted whereas in Al₂O₃, the chain is perpendicular to the surface (A. Ulman, Chem. Rev. 96 (1996) 1533).
Figure 8. Derivative of raw helium atom reflectivity signal as a function of temperature for hexanethiol on Au(111). Low temperature peak which changes with chain length corresponds to physisorption and the high temperature peak which is unaffected by the chain length variation corresponds to the chemisorbed state. (F. Schreiber, A. Eberhardt, T. Y. B. Leung, P. Schwartz S. M. Wetterer, D. J. Lavrich, L. Berman, P. Fenter, P. Eisenberger and G. Scoles, Phys. Rev. I 57 (1998) 12476.).
Figure 9. STM image of octanethiol on Au(111). Figure 10B is the plot of cross section labeled B in figure 10A running along the Au nearest neighbour direction. C and D are cross sections of plots of figure 10A along the Au next-nearest-neighbour directions. (G. E. Poirier, M. J. Tarlov, Langmuir 10 (1994) 2853).
Figure 10. (a) Various steps during the formation of self assembly. Gold coated glass slide is dipped in an ethanolic solution of thiol. The initial chemisorption process is very fast. This is followed by a slow step during which organization happens which takes several hours. (b) Structure of organized monolayer using a space filling model.
Figure 11. Docosanethiol on Au (111). The three regions indicate the three steps during the growth process. (Schreiber, F. Pro. Sur. Sci. 2000, 65, 151). Intensity of the features is plotted as a function of immersion time.
Figure 12. Constant current STM topographs showing the growth of mercaptohexanol monolayer from gas phase on Au (111) surface. (A) Clean Au (111) surface. (B) Stripped phase islands, (C) striped phase growth, (D) stripped phase growth showing Au vacancies, (E) growth of standing up phase at the cost of the stripped phase and (F) standing up phase growth at saturation limit. (Schreiber, F. Pro. Sur. Sci. 2000, 65, 151).
Figure 13. Various phases that can exist on a metal surface. Corresponding lattice structure, area per molecule and surface coverage has also been given. (Schreiber, F. Pro. Sur. Sci. 2000, 65, 151).
Figure 14. Molecular recognition by a monolayer of resorcinol on Au (111) surface. The receptor site showed high selectivity to perchloroethylene when dosed with a mixture of halocarbons (Schreiber, F. Pro. Sur. Sci. 2000, 65, 151).
Figure 15. An approach used to achieve enzyme immobilization. E is an enzyme.
Figure 16. Mechanism of opening and closing of ion channels by gramicidin. Gramicidin (in green) moves on the membrane and locking of two units opens the ion channel.
Figure 17. Schematic illustration of the ion channel based bio sensor. (B.A. Cornell, V. L.E Braach-Maksvytis, L.G. King, P. D. J. Osman, B. Raguse, L. Wieczorek, and R.J. Pace, Nature 387 (1997) 580). When MG and IG coincide, a large increase in ionic conductivity is observed a gramicidin ion channel opens up (a). When the analyte blocks the antibody fragments, movement of gramicidins becomes impossible, reducing the ionic conductivity (b).
Figure 19. Schematic showing a monolayer which changes conformation with applied electric field. As a result of this, the polarity of the surface can reversibly be switched by changing the electric field. This allows one to control the wetting behaviour of metal plates (J. Lahann, S. Mitragotri, T. Tran, H. Kaido, J. Sundaran, S. Hoffer, G. A. Somorjai and R. Langer, Science, 299 (2003) 371 ).
Figure 20. Experimental approach for making electrical contact to a nanoparticle
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