Current Opinion in Colloid & Interface Science 14 (2009) 157 – 168

Current Opinion in
COLLOID and
INTERFACE SCIENCE

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Self-assembly of organic molecules at metal surfaces

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Received 8 October 2007; received in revised form 2 January 2008; accepted 3 January 2008

Abstract

Self-assembly represents a promising strategy for surface functionalisation as well as creating nanostructures with well-controlled, tailor-made properties and functionality. Molecular self-assembly at solid surfaces is governed by the subtle interplay between molecule–molecule and molecule–substrate interactions that can be tuned by varying molecular building blocks, surface chemistry and structure as well as substrate temperature.

In this review, basic principles behind molecular self-assembly of organic molecules on metal surfaces will be discussed. Controlling these formation principles allows for creating a wide variety of different molecular surface structures ranging from well-defined clusters, quasi one-dimensional rows to ordered, two-dimensional overlayers. An impressive number of studies exist, demonstrating the ability of molecular self-assembly to create these different structural motifs in a predictable manner by tuning the molecular building blocks as well as the metallic substrate.

Here, the multitude of different surface structures of the natural amino acid cysteine on two different gold surfaces observed with scanning tunnelling microscopy will be reviewed. Cysteine on Au(110)-(1×2) represents a model system illustrating the formation of all the above mentioned structural motifs without changing the molecular building blocks or the substrate surface. The only parameters in this system are substrate temperature and molecular coverage, controlling both the molecular adsorption state (physisorption versus chemisorption) and molecular surface mobility. By tuning the adsorption state and the molecular mobility, distinctly different molecular structures are formed, exemplifying the variety of structural motifs that can be achieved by molecular self-assembly.

Keywords: Self-assembly; Organic molecules; Cysteine; Thiol; Metal surfaces; Scanning tunneling miscroscopy

1. Introduction

Modern material science is based upon providing smart solutions to a wide range of different applications in very heterogeneous environments. Ideally, functional materials should be tailored to address specific tasks and to provide well-defined functionality such as molecular recognition for (bio)sensors or protective layers for surface coatings [1].

Molecular self-assembly has been recognised as a very promising strategy for creating such tailor-made functional materials. Especially at solid surfaces, extended, two-dimensional molecular layers are already widely used, providing well-controlled properties such as corrosion resistance, surface superhydrophobicity, or antifouling coatings [2–4].

However, molecular self-assembly bears the potential for engineering much more advanced structures with high degree of complexity. Recently it has been demonstrated that molecular self-assembly can be employed to fabricate surface structures ranging from clusters [5•], unidirectional rows [5•,6•,7] to porous networks with well-defined pore size and periodicity [8••,9•] or arrays of metal atoms [10••]. This exceptional flexibility opens up another emerging field of application, namely molecular electronics that is believed to be the successor of today's electronics based on silicon technology: As early as 1965 Moore has stated his famous "Moore's law" [11], predicting that the growing demand for cheap, small, but yet faster computers and other electronic devices will inevitably result in the end of the "silicon road" [12] as the needed miniaturisation of integrated circuits is limited to several tens of nanometres using conventional silicon technology based on so-called "top-down" lithography [13]. A promising solution to

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doi:10.1016/j.cocis.2008.01.001

this challenge is integrating functional molecules into silicon devices as building blocks for e.g. wires, switches and transistors using "bottom-up" techniques. Nowadays, advances in chemistry synthesis allow to tailor the atomic structure of organic molecules providing a very wide range of flexibility in electronic structure. However, there is still a considerable gap between synthesising individual molecules with tailored electronic structure and an electronic circuit that can be addressed and connected to other devices. Besides the question of creating an interface to the macroscopic world, one of the main challenges for molecular electronics is to precisely position the molecular building blocks such that they eventually form a functioning structure like wires and logic operators. Manipulation of individual molecules one-by-one seems at present far too time-consuming to constitute a rational pathway for mass production of molecular electronic devices. Therefore, a technique that provides a route for creating molecular cluster, one-dimensional wires and even more complex structures in a predictable and well-controlled manner is of outmost importance for the evolution of molecular electronics. In contrast to addressing each molecule individually, employing molecular self-assembly has been identified as one of the few promising strategies for the mass fabrication of complex molecular systems [14,15•,16].

In order to take advantage of this versatile technique, a precise understanding of the mechanisms behind self-assembly is needed to enable the fabrication of well-defined molecular structures in a predictable manner. Consequently, molecular self-assembly has been studied extensively in the last decade. Many of these studies have been carried out on single crystal metallic or semiconducting surfaces with scanning tunnelling microscopy (STM) under ultra-high vacuum (UHV) conditions, as several central structuring motifs are experimentally accessible only when studied under clean and very precisely controlled UHV conditions. However, a growing number of publications emerge demonstrating a high degree of control in molecular self-assembly at the liquid–solid interface as well, especially on highly oriented pyrolytic graphite (HOPG) [17•,18].

In this review, the basic principles explaining molecular self-assembly on metal surfaces under UHV conditions will be summarised. These principles will be illustrated using cysteine on gold as a model system, demonstrating how distinctly different structures ranging from clusters and dimers, quasi one-dimensional rows to two-dimensional overlayers can be achieved by changing the substrate temperature and the molecular coverage.

2. Basic principles

Molecular self-assembly has been defined as the "spontaneous assembly of molecules into structured, stable, non-covalently joined aggregates under equilibrium" [19•]. This definition comprises the existence of predefined building blocks that interact weakly in order to provide the possibility for both bond formation and bond breaking until the stable equilibrium structure is formed. In contrast, in many experimental studies the system may not be able to reach the equilibrium state but might be trapped in a kinetically limited state. The term self-organisation has been established for such kinetically limited systems [15•]. The difference between molecular self-assembly and self-organisation is illustrated in Fig. 1: To distinguish between self-organisation and self-assembly the ratio between molecular flux and surface diffusivity needs to be considered. If the flux is high and diffusivity is low, the molecules are not able to reach their equilibrium structure, but rather get trapped in a diffusion-limited state, as demonstrated by the growth of dendrimeric Ag islands on Pt(111) [20]. On the other hand, if the flux of molecules is low and the diffusivity is high, the molecules are able to move freely on the surface, resulting in the growth of the thermodynamically favoured, equilibrium structure.

The structure formation is governed by the balance between intermolecular and molecule–substrate interactions as illustrated in Fig. 2a. The diffusivity of the molecules on the surface can be controlled by a variation of substrate temperature. Upon increasing the substrate temperature, thermal energy is transferred to the molecules, thereby providing sufficient kinetic energy E_{kin} to overcome the diffusion barrier E_{d} on the surface (see Fig. 2b). This is one prerequisite for the formation of the thermodynamic equilibrium structure. On the other hand, the kinetic energy of the molecules E_{kin} must, of course, not exceed the binding energy E_{b} of the molecules on the surface - otherwise the molecules would desorb from the surface. Finally, we need to consider the intermolecular interaction energy E_{inter}. This interaction is crucial for the formation of ordered structures as it comprises the information on how to assemble the predefined building blocks. As mentioned above, the intermolecular interaction should be "weak", meaning that the molecular entities must possess sufficient energy to probe the corrugation of the energy landscape in order to identify the equilibrium structure in the global minimum. If the intermolecular interaction is "strong" the molecules stick together irreversibly once they have met, preventing the formation of an ordered equilibrium structure. On the other hand, the interaction between the molecules must be of sufficient strength to allow for the formation of a stable structure. The latter condition can be achieved when the intermolecular interaction energy E_{inter} is of the same order as the kinetic energy of the molecules E_{kin}, being only slightly larger than E_{kin}. The energy conditions to be fulfilled for molecular self-assembly can therefore be summarized as $E_{\mathrm{b}} > E_{\mathrm{inter}} \geq E_{\mathrm{kin}} > E_{\mathrm{d}}$.

An additional aspect needs to be considered when the molecules can both physisorb and chemisorb on the surface as depicted in Fig. 3. Usually diffusion barriers become very large when molecules chemisorb onto the surface as chemisorption is stronger than physisorption (Fig. 3a). An ordered structure of chemisorbed molecules on a substrate surface is, therefore, usually not governed by intermolecular interactions but solely by the strong chemisorption energy. This is why covalently bound molecules are usually not considered as molecular self-assembled structure, but rather as a "classical" superstructure (typical examples are atoms or small molecules like oxygen or carbon monoxide on various metal surfaces forming regular