SELF-ASSEMBLED MONOLAYERS OF CALIX[n]ARENE (n=4,6) DERIVATIVES ON SI(100) AND POLYCRYSTALLINE COPPER

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The controlled production of organic monolayers on semiconductor and metal surfaces of technological interest can provide a material with new features in the nanoscale. While numerous examples have been already proposed of functional species, such as redox couples, bio-molecules or selective receptors anchored on silicon or on gold surfaces, very rarely a close comparison has been reported of the behaviour of one class of such compounds on both a semiconductor and a metal surface. In this framework, the first compared study is given here of the distinct anchoring properties on H-Si(100) and polycrystalline Cu of a few members of a class of molecules, chosen among the most representative ones in supramolecular chemistry: calix[n]arenes.[1]

A covalent functionalization on both Si and Cu surfaces requires the molecules to be differently modified: a thiol (-SH) or C=C termination are respectively suitable for copper or H-Si(100). Anchoring on Cu was reached by dipping a clean sample in a calix[n]arene-SH solution (n = 4,6), while a wet chemistry recipe was followed for Si(100), combined with an extra-mild photochemical activation via visible light.[2] Molecular adhesion onto either surfaces has been demonstrated by the presence of XPS signals from specific elements in the molecules: the aromatic nuclei of the calix[n]arene derivatives designed for H-Si were functionalized with Br atoms or NO_2 groups, while the S atom was used as the molecular identifier on Cu. AFM measurements performed on H-Si(100)/calix[4]arene have revealed structures 2-2.5 nm high, consistent with the length of the molecule in a "standing up" conformation. The diameter of these structures suggests that self-assembled calixarenes clusters are formed on Si.

A further extension on Cu is represented by anchoring a rotaxane.[3] A pseudorotaxane species was formed in solution by reacting a calix[6]arene "wheel", functionalized with three *N*-phenylurea groups on its upper rim, with a viologen (4,4'-bipyridinium) axle.[4] The resulting species has been anchored on Cu via the thiol termination of the axle. This two-step reaction has produced a threaded rotaxane covalently bound to Cu surface, as shown by XPS results. This species is ready to respond to external stimuli.

References:

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