

Electrochemical and SPM characterisation of self-assembled molecular junctions

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Electrical nanodevices that contain a molecule as the active element have attracted the interest of many research groups. Electron transport through a single molecule is a challenging scientific topic. In addition, molecular junctions may form the basis for future transistor-type nanodevices. There are two ways to form a molecular junction. A molecule can be mounted between two electrodes separated by a gap in the 1 nm range. Alternatively, molecules can be anchored on a macroscopic substrate using self-assembly, the other end of the molecule can be bound to metallic or semiconducting nanodots [1,2][Fig. 1]. This method leads to a huge number of parallel molecular junctions. The nanostructured metal/SAM/dot structure can be investigated by macroscopic (electrochemical) methods, while individual molecular junctions can be addressed by contacting the nanometal with the tip of a Scanning Tunnelling Microscope (STM). Oligo(cyclohexylidene) molecules have interesting transport properties; it has been shown that they possess strong through-bond orbital coupling and that they form well-ordered SAMs on gold surfaces [2].

We prepared gold/oligo(cyclohexylidene)/nanodot junctions using self assembly and electrochemistry and characterised this architecture by AFM. The electrical properties of this nanostructured interface were investigated by electrochemical methods.

- I. Self-assembled monolayers of S-terminated oligo(cyclohexylidene) were prepared on flame-annealed gold (1,1,1) surfaces. The quality of these layers was checked by electrochemical capacitance measurements, cyclic voltammetry and AFM/STM. S-terminated oligo(cyclohexylidene) molecules form well-ordered rigid SAMs which suppress electron

transfer of $\text{Fe}(\text{CN})_6^{3-/4-}$.

- II. We anchored 20 nm-sized gold nanodots on this molecular layer by placing the gold/SAM substrate in an electrochemical cell containing an aqueous solution of charge-stabilised gold colloids [Fig.2]. We found that at open-circuit or slightly positive potentials with respect to SCE a sub-monolayer of individual nanodots attach to the SAM (via Au-S bonding). At negative potentials, attachment of individual particles does not occur. The attachment kinetics of the nanoparticles can be followed in-situ by measuring the amount of nanodot charging/decharging and by ex-situ tapping-mode AFM.
- III. The electron transfer properties of oligo(cyclohexylidene) spacer molecules were studied by investigating the dynamics of gold nanoparticle charging/decharging in the gold-substrate/spacer/nanodot electrochemical interface. Electrical measurements on individual molecular junctions are in progress.

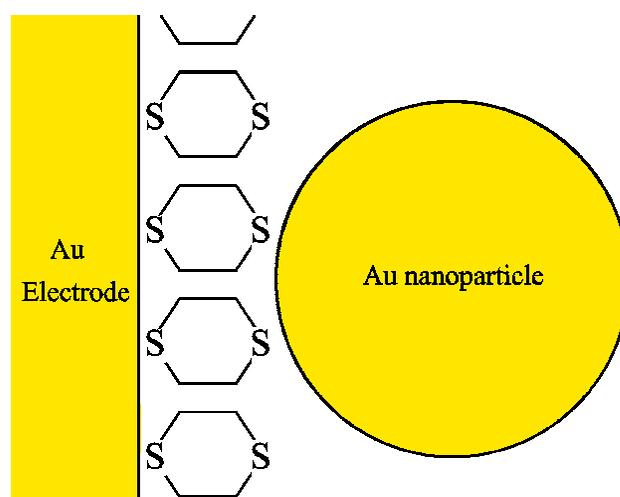


Fig. 1: Example of a Nanoparticle bound to an electrode surface by a SAM.

References:

- [1] A.N. Shipway *et al.*, ChemPhysChem 1 (2000) 18
- [2] E.P.A.M. Bakkers *et al.*, Angew. Chem. Int. Ed. 39 (2000) 2385

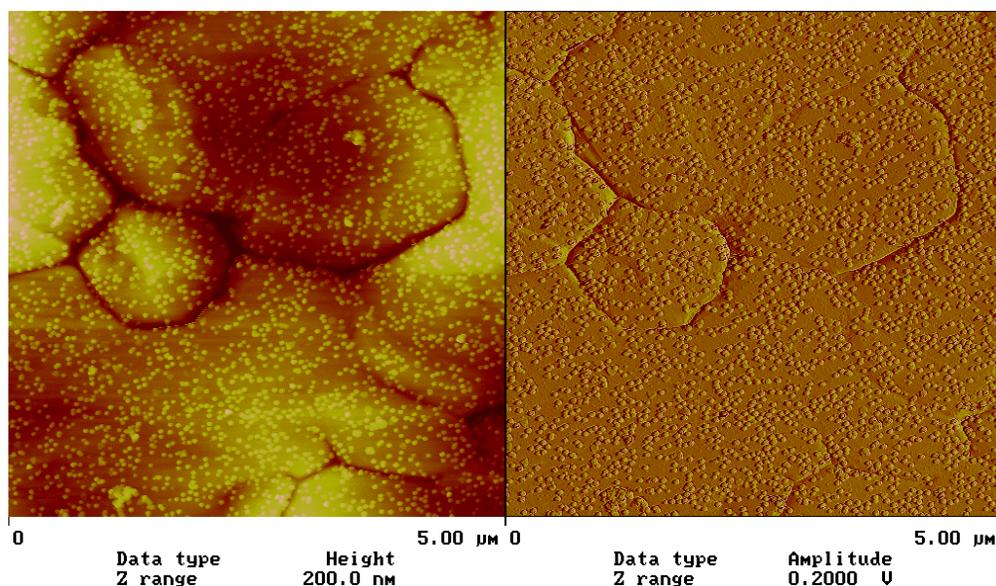


Fig. 2: Tapping mode AFM image of 20 nm charge stabilised Au nanoparticles deposited on a Au(111) surface derivatised with a SAM.