ElecMol20
14-17 December 2020
ENS de Lyon
10th International Conference on Molecular Electronics

Coupling plasmonic trapping and single-molecule junctions

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Abstract:

Molecular electronics (ME) is largely based on the understanding of the properties of single molecules (SM) to enable their detailed characterization. Such knowledge is aimed to define molecular properties in future implementation on molecular-based devices. Nowadays, the detection of individual molecules trapped between two electrodes[1] is a reality, and different approaches have been developed for high-precision SM trapping in fixed size nanogaps.[2] They permit from electrical characterisation of individual molecules to molecular sensing, recognition, or SM reactions.[2,3] These trapping approaches are based on the detection of SM events with lifetimes that last for a characteristic time rather short - in the order of a fraction of milliseconds - due to thermally activated junction breaking. Hence, elaborated junction characterisation is hindered over longer timescales. The detection of short junction lifetimes limits any fundamental study and therefore, immobilising molecules for prolonged timescales has remained one of ME's central challenges.

In the first block, we will present our recently reported plasmon-supported break-junction technique (PBJ)[4] based on scanning tunnelling microscopes working with the break-junction mode (STM-BJ).[1] Our PBJ technique significantly increases the lifetime of SM junctions preserving the target molecule's native structure and contact geometry. In PBJ, the exerted optical (stabilising) force of the nearfield gradient is exploited to increase the trapped molecule junction stability, without the need for chemical modification of the target molecule and/or electrode. The optically induced mechanical stabilization of the trapped molecule is suitable at low and moderate far-field power densities and successfully overcomes the native stochastic disconnection of the junction, imposing a deterministic lifetime.

In the second block, we will explain how the steering of two physical features can extend the effectiveness of the nearfield trapping[5] in the PBJ: (i) the target molecule's optical resonance and (ii) the localised surface plasmon resonance (LSPR) energy of the nanogap. Our target molecule, the metalloprotein Azurin (Azu), has a Cu(II) metal centre that when oxidised possesses an intense absorption ligand-to-metal charge transfer band, resonant to the employer laser frequency to excite the Au plasmon. Thanks to the electrochemical (EC) gating capabilities of our approach, we can tune the resonant excitation conditions of the trapped Azu via modifying its Cu centre's redox state. Consequently, when Azu is oxidised presents resonant conditions, and therefore, its electric polarizability is enhanced. Since the emerging gradient force of the nearfield is proportional to the polarizability, the higher is the polarizability, the larger is the efficiency of the molecular trapping. In parallel, the tuning of the nanogap's LSPR energy can be also used to enhance the molecular trapping. LSPR energy profile depends on the applied electrode potential determined by the Fermi level displacement which we control via the EC gate. The LSPR energy profile is correlated with the wavelength-dependent electric field enhancement that controls the nearfield exerted force, and thus tunes the optical trapping efficiency and junction lifetime. Our results demonstrate that the optical trapping of individual molecules is suitable, and hence it enhances the molecular sensing and recognition.

References:

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