Redox state-modulated electron transport properties of polyoxometalates at the nanoscale

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Polyoxometalates (POMs) are nanometric molecular oxides with remarkable redox properties that can be explored in the context of advanced components [1-3]. We propose to develop scalable functionalities in 2D nanomaterials based on POMs (2D-PN, 2D POM Network) "programmable/switchable" on demand thanks to the multifunctional properties of these molecules (e.g. multiredox states). The first objective is to prepare compact and dense monolayer of POMs on a metal substrate to assess their electron transport (ET) properties. Here, we report the ET properties of those POMs (here $[PMo_{12}O_{40}]^{3-}$ and $[NaP_5W_{30}O_{110}]^{14-}$) in their different redox states using self-assembled monolayers (SAM) and conductive-AFM (Figure 1). For both molecules, we clearly observed an increase of the conductance for the reduced states which is related to a decrease of the energy of the molecular orbital involved in the transport though the metal/POM/metal junction : from ≈0.65 eV to ≈0.43 eV for PMo_{12} and from ≈0.44 eV to ≈0.31 eV for P_5W_{30}. We tentatively ascribe this feature to a change from a LUMO mediated ET to a HOMO mediated ET after reduction (ab-initio calculations in progress). Then, we successfully fabricated multi-connected (6 electrodes) hybrid 2D-PN with $[PMo_{12}O_{40}]^{3-}$ and Au nanoparticles (Figure 2) and we measured their ET revealing large variability in the 2D-PN. Preliminary low-frequency noise and high-harmonic generation measurements will be used to discuss the possible use of these 2D-PN within the global framework of the physical implementation of a neuromorphic reservoir computing system with nano-objects (CNT, nanoparticles, molecules, atomic switches).[4-7]

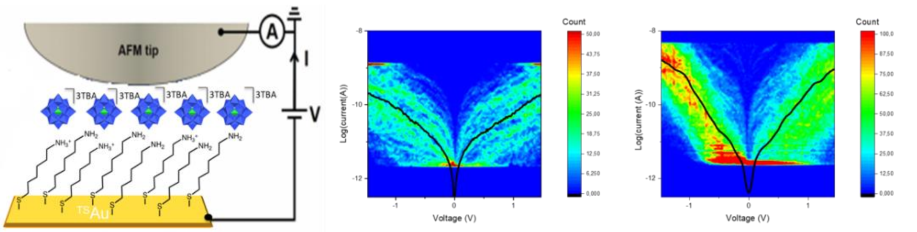

Figure 1 : General scheme of the electronic transport characterization by C-AFM of the $[PMo_{12}O_{40}]^{3-}$ electrostatically deposited onto alkylamine SAM functionalized gold surface and histogram of the current-voltage curves (I-V) in oxidized state (left) and after one electron reduction (right).

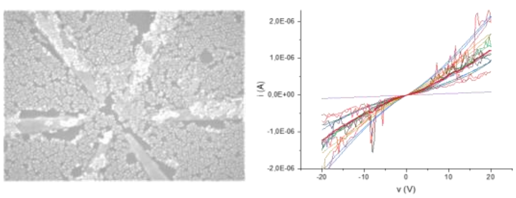

Figure 2 : SEM images (left) and current-voltage curves (I-V) (right) of fabricated multi-connected hybrid 2D-PN with $PMo_{12}O_{40}$ and Au nanoparticles

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