Report on the outcomes of a Virtual Mobility[1]

Action number: CA20129

Grantee name: Alexey Verkhovtsev

Virtual Mobility Details

Title: Atomistic modelling of the Photo-Assisted Chemical Vapour Deposition (PACVD) process

Start and end date: 12/08/2024 to 30/09/2024

Description of the work carried out during the VM

The work carried out during this virtual collaboration followed the research plan presented in the grant application. The work was carried out in collaboration with Mr. Cauê Paula De Souza and Dr. Felipe Fantuzzi from the School of Chemistry and Forensic Science, University of Kent, Canterbury, UK.

(i) *Construction and atomistic characterisation of self-assembled monolayers on oriented Au(100) and Au(111) surfaces*.

Self-assembled monolayers (SAMs) made of thiolated carbon-based polymer molecules (consisting of repeating C_2H_4 units) deposited on flat gold surfaces have been characterised using the classical molecular dynamics (MD) approach. The particular molecules considered are made of a 16-carbon long alkanethiol (thiolated hexadecane, $C_{16}H_{32}S$) terminated with either COOH (carboxylic acid), OH (hydroxyl) or H (simple hydrocarbon chain), see Fig. 1. At the other end of the molecule, the hydrogen atom has been removed from the thiol group to allow the ligands to be covalently attached to the gold surface by the formation of Au-S bonds.

The geometry of the free ligands was first optimised using density functional theory (DFT), and the optimised geometry was used to obtain the parameters of the CHARMM molecular mechanics force field using the SwissParam and ParamChem (CGenFF) engines.

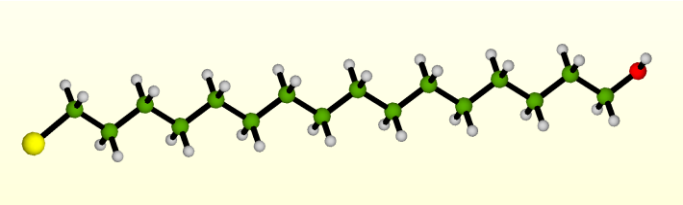

Figure 1. Geometry of a thiolated hexadecane molecule functionalized with an OH group ($C_{16}H_{33}OS$), which has been used to create a polymer-based SAM.

The ligand molecules were deposited on a few-nanometer thick gold slab made of five atomic layers. Two surface orientations, namely Au(100) and Au(111), were considered. A cubic box of regularly distributed

[1] This report is submitted by the grantee to the Action MC for approval and for claiming payment of the awarded grant. The Grant Awarding Coordinator coordinates the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

ligand molecules with a surface density of ~4.7 molecules per nm^2, corresponding to experiments [1], has been created. The systems were created using the MBN Studio software [2] following the computational approach described in Refs. [3,4], where the computational structural characterisation of gold nanoparticles and flat gold surfaces coated with polyethylene glycol (PEG) ligands was performed. The parameters previously used for the simulation of Au@PEG systems were compared with those derived for the simulation of alkanethiol SAMs on flat gold surfaces.

The classical MD simulations were performed using the MBN Explorer software package [5]. The geometry and morphology of the created SAMs were characterised by studying different sets of molecular force field parameters from the Chemistry at Harvard Molecular Mechanics (CHARMM) and the Universal Force Field (UFF).

(2) *Obtaining reactive force field parameters from quantum chemistry calculations*.

Parameters of the reactive rCHARMM force field [6] for several Ru-containing organometallic molecules relevant to the PACVD experiments [1,7,8] were obtained by means of DFT calculations. Relaxed potential energy scans for the stretching of different covalent bonds in the considered molecules were performed to determine the equilibrium bond distances, bond force constants and bond dissociation energies. The molecular topology models for the isolated Ru-based precursors were created using the rCHARMM force field.

[1] B.G. Salazar, C.R. Brewer, L. McElwee-White, A.V. Walker, *J. Vac. Sci. Technol. A* **40** (2022) 023404

[2] G.B. Sushko, I.A. Solov'yov, A.V. Solov'yov, *J. Mol. Graph. Model*. **88** (2019) 247

[3] A.V. Verkhovtsev, A. Nichols, N.J. Mason, A.V. Solov'yov, *J. Phys. Chem. A* **126** (2022) 2170

[4] M.D. Dickers, A.V. Verkhovtsev, N.J. Mason, A.V. Solov'yov, *Eur. Phys. J. D* **77** (2023) 141

[5] I.A. Solov'yov, A.V. Yakubovich, P.V. Nikolaev, I. Volkovets, A.V. Solov'yov, *J. Comput. Chem*. **33**, 2412 (2012)

[6] G.B. Sushko, I.A. Solov'yov, A.V. Verkhovtsev, S.N. Volkov, A.V. Solov'yov, *Eur. Phys. J. D* **70**, 12 (2016)

[7] K.R. Johnson, P. Arevalo Rodriguez, C.R. Brewer, J.A. Brannaka, Z. Shi, J. Yang, B. Salazar, L. McElwee-White, A.V. Walker, *J. Chem. Phys*. **146** (2017) 052816

[8] C.R. Brewer, N.C. Sheehan, J. Herrera, A.V. Walker, L. McElwee-White, *Organometallics* **41** (2022) 761

Description of the VM main achievements and planned follow-up activities

The planned goals and expected results of this virtual collaboration have been achieved. The main results obtained are: (i) the atomistic characterisation of the structure of alkanethiol SAMs on gold surfaces and (ii) the determination and validation of the rCHARMM force field parameters for the considered Ru-based precursors.

Regarding part (i), particular attention was paid to the analysis of the tilt angle of the ligand molecules, i.e. the angle that the carbon chain makes with respect to the normal to the surface. It was found that the ligand tilt angle is very sensitive to the chosen set of force field parameters, in particular to the values of the atomic partial charges. Different sets of parameters and partial charges were explored to find the best set that reproduced the experimentally determined angle of 30 degrees for the ligands with respect to the vector normal to the surface, see Fig. 2.

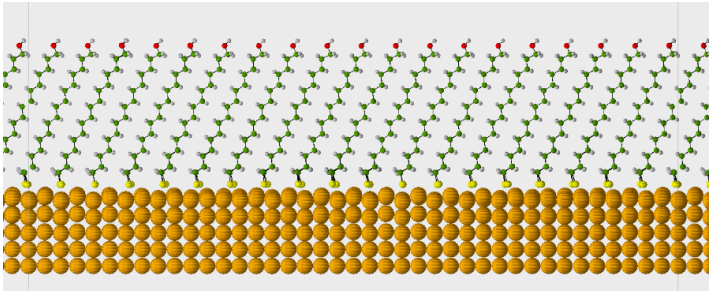

Figure 2. Structure of a SAM made of functionalized hexadecane molecules ($C_{16}H_{33}OS$) deposited onto a gold surface.

Regarding part (ii), the rCHARMM force field parameters generated from the DFT-based potential energy scans and the created molecular topologies for the studied Ru-based precursors have been validated by structure optimisation and MD simulations of the dynamics and thermal stability of isolated molecules at different temperatures in the range of 300 to 1000 K.

The results obtained will be described in a joint publication, which is currently in preparation.

The computational steps performed during this VM will form the basis for the subsequent simulations of irradiation-driven modifications of the created polymer layer under exposure to radiation and simulations of the PACVD process using the irradiation-driven molecular dynamics method.