Electronic Supplementary Information

Thermodynamics of the physisorption of capping agents on silver nanoparticles

Matías Zúñiga-Bustos

Programa Institucional de Fomento a la Investigacion, Desarrollo e Innovacion (PIDi), Universidad Tecnologica Metropolitana, Santiago 8940577, Chile.

Center for Bioinformatics and Molecular Simulation, Facultad de Ingenieria, Universidad de Talca, 2 Norte 685, Talca, Chile.

Jeffrey Comer

Department of Anatomy and Physiology, Kansas State University, Manhattan, Kansas, 66506-5802.

Horacio Poblete

Center for Bioinformatics and Molecular Simulation, Facultad de Ingenieria, Universidad de Talca, 2 Norte 685, Talca, Chile.

Millennium Nucleus of Ion Channel-Associated Diseases (MiNICAD),Talca, Chile.

E-mail: hopoblete@utalca.cl

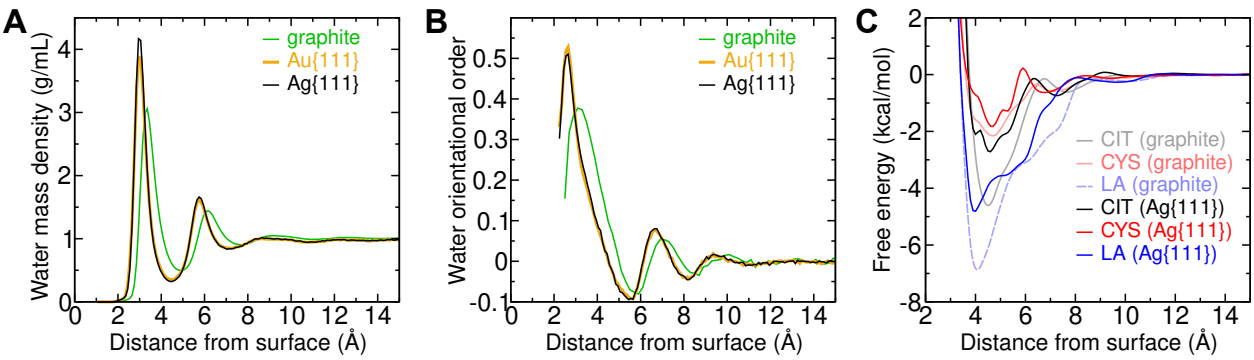

Figure S1: Comparison between silver–water interfaces and aqueous interfaces with other materials. (A) Mass density of water as a function of distance from graphite basal plane, Au{111}, and Ag{111} surfaces, modeled with the CHARMM General Force Field,[1–3] GolP-CHARMM,[4] and AgP-CHARMM,[5] respectively. (B) The orientational order parameter $\frac{1}{2}(3\cos^2\theta - 1)$ of water molecules as a function of distance from the graphite, Au{111}, or Ag{111} surfaces. Here, θ is the angle between the z-axis (perpendicular to the surfaces) and the normal to the plane of the three atom centers of each water molecule. (C) Free energy as a function of distance between the surface layer of a solid material and the center of mass of a solute. The solutes are citrate in doubly-protonated -1 form (CIT), cysteine in zwitterionic form (CYS), and lipoic acid in deprotonated -1 form (LA).

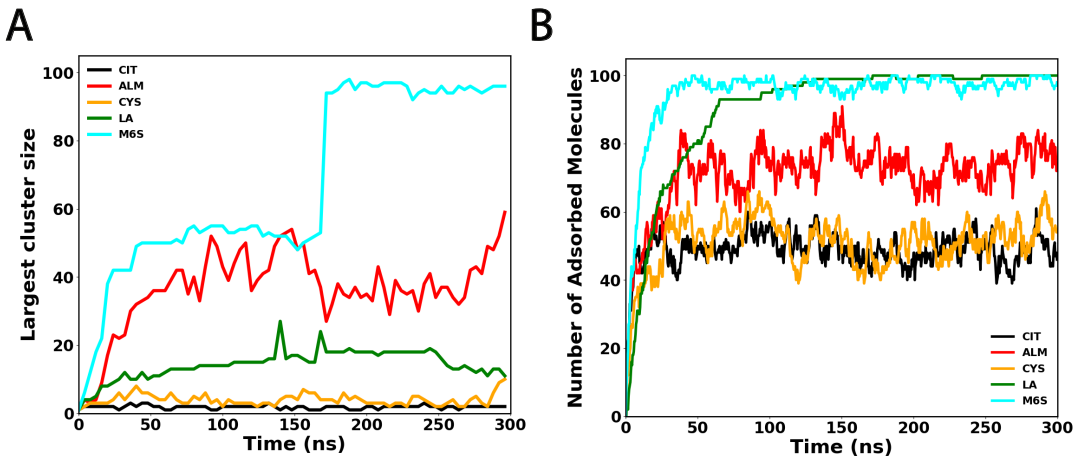

Figure S2: (A) Number of capping molecules in the largest surface-bound cluster on the Ag{111} surface for a simulation of 100 capping molecules. (B) Number of molecules adsorbed to the silver surface in the same simulation. Molecules that are not adsorbed to the surface cannot form surface-bound clusters.

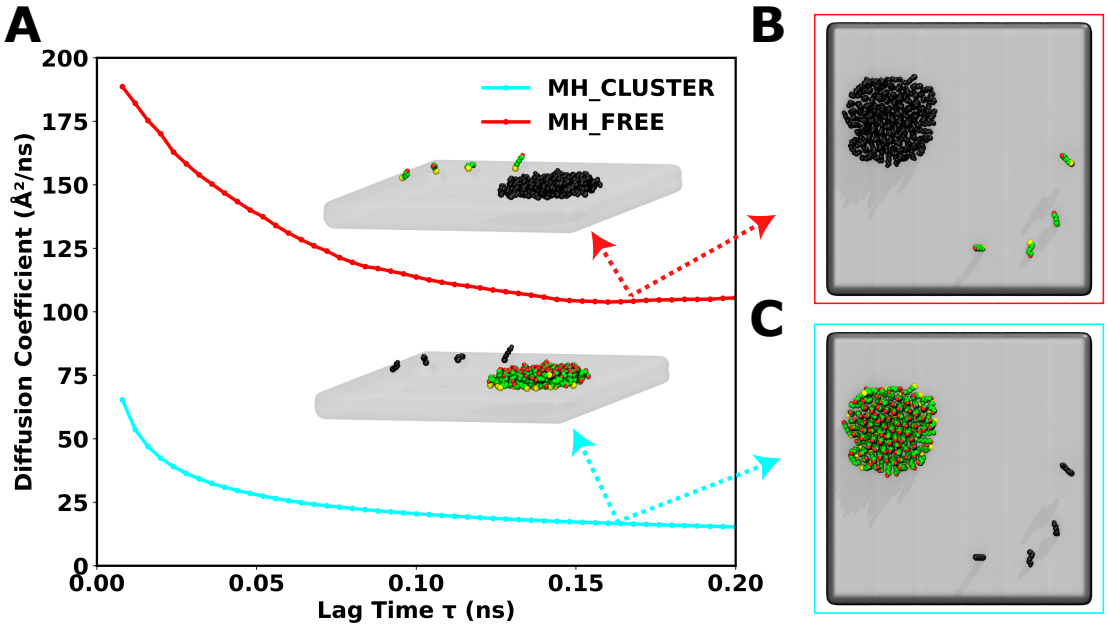

Figure S3: Estimation of the diffusion coefficient. (A) Diffusion Coefficient of MH molecules calculated in both cluster and free states as a function of lag time. (B) Representative snapshot for the identification of free MH molecules. (C) Representative snapshot for the identification of MH molecules that have already formed a cluster on top of the surface.

References

1. Vanommeslaeghe, K.; Hatcher, E.; Acharya, C.; Kundu, S.; Zhong, S.; Shim, J.; Darian, E.; Guvench, O.; Lopes, P.; Vorobyov, I.; MacKerell, A. D. CHARMM General Force Field: A Force Field for Drug-like Molecules Compatible with the CHARMM All-atom Additive Biological Force Fields. *J. Comput. Chem.* **2010**, *31*, 671–690.
2. Comer, J.; Chen, R.; Poblete, H.; Vergara-Jaque, A.; Riviere, J. E. Predicting Adsorption Affinities of Small Molecules on Carbon Nanotubes Using Molecular Dynamics Simulation. *ACS Nano* **2015**, *9*, 11761–11774.
3. Azhagiya Singam, E.; Zhang, Y.; Magnin, G.; Miranda-Carvajal, I.; Coates, L.; Thakkar, R.; Poblete, H.; Comer, J. Thermodynamics of adsorption on graphenic surfaces from aqueous solution. *Journal of chemical theory and computation* **2018**, *15*, 1302–1316.
4. Wright, L. B.; Rodger, P. M.; Corni, S.; Walsh, T. R. GolP-CHARMM: First-principles Based Force Fields for the Interaction of Proteins with Au (111) and Au (100). *J. Chem. Theory Comput.* **2013**, *9*, 1616–1630.
5. Hughes, Z. E.; Wright, L. B.; Walsh, T. R. Biomolecular adsorption at aqueous silver interfaces: first-principles calculations, polarizable force-field simulations, and comparisons with gold. *Langmuir* **2013**, *29*, 13217–13229.