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ESI for First principles characterisation of bio-nano interface

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In Table S1 we present details of the band gaps and ionization potentials calculated using SIESTA [18] performed to validate the DFT calculations.

Table S1: Band gaps and ionization potentials as a function of the number of K points for the anatase and rutile forms of TiO_2 and cells calculated using the SIESTA code.[18]

TiO2 Solid systems	K points	Band gap (eV)	ionization potential – VBM energy (eV)
Anatase	(1/1/1)	2.90	8.64
		2.72	9.05
		2.50	8.80
		2.73	8.86
		2.38	8.71
		2.49	8.79
		2.38	8.69
		2.42	8.75
		2.39	8.68
	(10/10/10)	2.39	8.72
Rutile	(1/1/1)	3.46	9.42
		1.48	9.00
		2.62	9.87
		2.52	9.65
		2.71	10.04
		2.65	9.89
		2.72	10.08
		2.70	9.99
		2.73	10.10
	(10/10/10)	2.71	10.04

Metadynamics calculations

For the computation of adsorption free energies and potentials of mean force of small molecules to nanomaterials surfaces we used the metadynamics (MetaD) methodology using the surface separation distance (SSD) as a collective variable. The SSD was determined as the distance between the sorbent center of mass, and the outermost layer of the surface atoms. The well-tempered MetaD approach[55] was implemented. The binding free energy of a molecule was calculated from a converged adsorption profile $F(s)$ with the estimator

$$\Delta F_{ads} = -k_B T \ln \left(\frac{1}{\delta} \int_0^\delta ds \; e^{-F(s)/k_B T} \right), \tag{S1}$$

where δ is the thickness of the adsorption layer. The result depends weakly (logarithmically) on this parameter so its exact value is not of high importance for the binding free energy. We used $d = 0.8$ nm in our calculations.

All computations have been carried out for systems containing 7000-8000 atoms in a 3-dimensional periodic box of the size about 3×3×8 nm, with 2-dimensional periodic TiO_2 slab in XY direction and about 1700 water molecules. Gromacs v2018.1[56] with PLUMED plugin v2.5[57] were used in all simulations. The TiO_2 slab was prepared by repeating the unit cell the necessary number of times, and undercoordinated surface Ti atoms were hydrated by either adsorbed water or hydroxyl groups in the ratio 70% to 30%. This fraction (30%) of hydroxyl groups provides surface charge of about $-0.65e$ nm^{-2} which corresponds to the experimentally measured surface charge of TiO_2 NPs at neutral pH.[58] The solute molecule was placed outside the material, and the remaining space in the simulation box was filled with water molecules (TIP3P model). The system was first energy-minimized for 10,000 steps using the steepest gradient method. Then the system was equilibrated in the NVT-ensemble simulations for 20 ps and in NPT-ensemble for 1 ns with time step 1 fs. The temperature was set to 300 K and pressure to 1 bar. Production simulations with metadynamics were carried out in NVT conditions, with established in preliminary NPT simulations volume, for 300 ns. A *v*-rescale thermostat with relaxation time 1 ps

was used to ensure correct ensemble fluctuations. The Particle-mesh Ewald method was used to treat both electrostatic and Lennard-Jones interactions outside the real-space cutoff 10 Å. The motion of the centers of mass of material and solvent were removed separately to avoid artificial flow of the system through periodic boundaries. In order to reduce time spent by the adsorbate in the bulk solvent far from the surface, visiting of such states was prevented by a soft wall potential:

$$U_{wall}(s) = k(s-a)^4 \qquad (S2)$$

with the force constant $k = 40$ kJ mol^{-1}·Å^{-4} and $a = 1.5$ nm.

PMFs for TiO$_2$ Anatase 101 and TiO$_2$ Rutile 110

Here, we present plots of the potentials of mean force (PMFs) calculated for the interaction between the biomolecular fragments and the two TiO$_2$ surfaces.

Protein binding energies

We also provide tabulated data of the calculated descriptors including binding energies for amino acids and a set of 40 proteins on titanium dioxide NPs (anatase(101) and rutile(110)) of a range of zeta potentials (-50 – +50 mV) and radii (5 – 200 nm), see file TiO2NP_Descriptors_40proteins.xslx.

Figure S1: Top: PMFs calculated from atomistic simulations for the various amino acids and lipid fragments against a slab of TiO$_2$ rutile (Miller index 110). Bottom: As top, except for the anatase (101) surface.
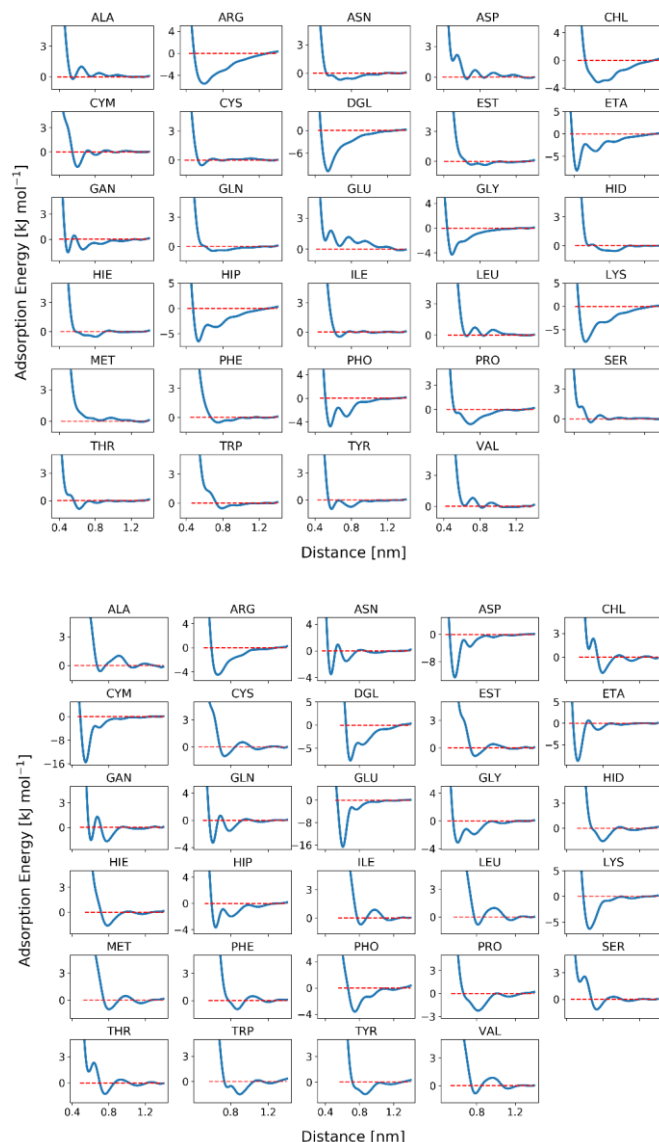
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