Proton Transfers at Dopamine-Functionalized TiO$_2$ Interface

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Despite the many successful synthesis and applications of dopamine-functionalized TiO$_2$ nanohybrids,[1,2,3] there is not yet an atomistic understanding of the interaction of this 1,2-dihydroxybenzene derivative ligand with the titanium dioxide surfaces.

In this work, based on a wide set of dispersion-corrected hybrid density functional theory (DFT) calculations[4] and on density functional tight binding (DFTB) molecular dynamics simulations,[5] we present a detailed study of the adsorption modes, patterns of growth and configurations of dopamine on the anatase (101) TiO$_2$ surface, with reference to the archetype of 1,2-dihydroxybenzene ligands, i.e. cathecol.[6]

At low coverage, the isolated dopamine molecule prefers to bend towards the surface, coordinating the NH$_2$ group to a Ti$_{5c}$ ion.

At high coverage, the packed molecules succeed in bending towards the surface only in some monolayer configurations. When they do, we observe a proton transfer from the surface to the ethyl-amino group, forming terminal NH$_3^+$ species, which highly interact with the O atoms of a neighboring dopamine molecule. This strong coulombic interaction largely stabilizes the self-assembled monolayer. Based on these results, we predict that improving the probability of dopamine molecules being free to bend towards the surface through thermodynamic versus kinetic growth conditions will lead to a monolayer of fully protonated dopamine molecules.
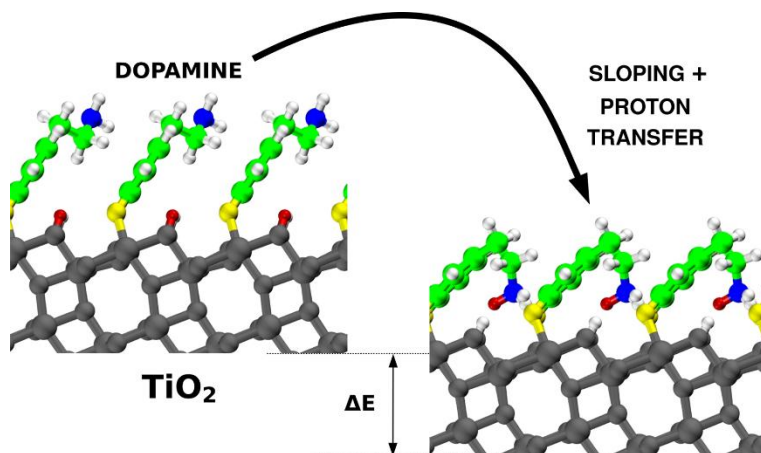
Figure 1 Proton transfer mechanism for one monolayer of dopamine molecules on anatase TiO$_2$ (101) surface

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