Dye and coadsorbent organization on anatase surfaces from atomistic simulation

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In a dye-sensitized solar cell (DSSC) the functions of light harvesting, charge separation and charge transport are separated. Light is harvested by a monolayer of dye molecules on the surface of a semiconductor, usually anatase type TiO_2. Characteristics of bonding, surface coverage and involvement of counterions are expected to control the rates of charge-transfer at the dye/TiO2 interface as well as of the undesirable charge recombination. Here we study the self-organization and bonding characteristics of two commonly used light harvesting dyes $[(C_4H_9)_4N]3[Ru(tcterpy)(NCS)_3]$ ("black dye"; where tcterpy = 4,4',4''-tricarboxy-2,2',2''-terpyridine) and Ru(dcbpy)2(NCS)2 ("N3"; where dcbpy = 4,4'-carboxylate-2,2'-bipyridyl) (N3, cf. [1]) on the most relevant surfaces of anatase type TiO_2, (101) and (001) by atomistic molecular dynamics (MD) simulations. For both dyes carboxyl groups are designed to bond to the TiO_2 surface, while thyocyanate groups are considered to collect electrons from the hole conductor in the dye regeneration process. In a second step the variation of the dye organization and surface coverage was investigated for a coadsorption of deoxycholic acid along with "black dye" molecules.

Experimental
Atomistic molecular dynamics simulations have been performed using the Universal Forcefield with QEq charges as implemented in the Materials Studio software suite. Simulations are based on supercells of anatase that contain a two-dimensionally continuous array of TiO_2 slabs ($53\times53\times19$ Å^3 for (001), $53\times57\times15$ Å^3 for (101)), separated by 30 – 50 Å gaps containing the dye molecules as well as counterions and coadsorbents, if applicable. The choice of forcefield and charging method was guided by the fact that QEq charges depend on the actual bonding geometry and thus are able to reproduce a charging of the TiO_2 slabs when dye molecules are adsorbed. Energy minimizations were conducted as NVE Quench MD simulations and preceded by MD simulations (at nominal temperatures of 500K – 1000K) to ensure that reorganizations of adsorbed dye molecules are possible and initial configurations have no influence on the results. The investigated anatase surfaces differ in that for (001) all Ti atoms on the surface are only 5-fold coordinated, while the (101) surface contains rows of fully (6-fold) coordinated and 5-fold coordinated Ti atoms, constraining the orientation of adsorbed dye molecules. As a simple tool to assess adsorption energies, we use the sum of bond valences (BV) of bonds between the dye and the surface, calculated using our recently developed softBV bond valence parameter set [2].

Results and Discussion
Based on our simulations preferred adsorption configurations for the different dye molecules on anatase (001) and (101) surfaces are identified and characterized. For low dye concentrations both types of dye molecules are found to bond preferably tripodally:

For "black dye" the most favorable configuration involves bonding contributions by two carboxyl groups plus one thyocyanato group. Individual N3 dye molecules bond on the (101) surface either via two carboxyl groups on the same bipyridine plus one thiocyanato sulfur, or via three carboxyl groups. The latter leads to only slightly stronger bonds (average sum of BVs 0.62 valence units), but bonding via 2 carboxyl groups plus one thiocyanato group (average sum of BVs 0.60 v.u.) is more commonly occurring for steric reasons. The (001) surface permits a wider range of tripodal dye adsorption configurations, but the average total adsorption strength (0.45 valence units) is significantly smaller and the contribution of S-Ti bonds to the adsorption significantly higher than on the (101) surface (45% compared to 19%), suggesting that (101) surfaces are more suitable for energy harvesting.

When in the simulations the "black dye" concentration is increased to values desirable for practical applications, the unfavorable bonding via NCS groups is reduced but not eliminated. In contrast to earlier simulations [3] we observe that under such circumstances "black dye" molecules typically bond via two carboxyl groups. Still nearly one half of the molecules form a third bond via a NCS ligand perpendicular to the terpyridine plane. 15% of the NCS groups are involved in significant interaction with surface Ti for the dominating (101) surfaces, 21% for (001) surfaces. Recent photoelectron spectroscopic data [4] accordingly suggest that 15% of the S are involved in Ti-S interactions. Similarly, for higher concentrations of N3 a distribution of three configurations involving one or two NCS ligands is observed.

Both investigated dyes differ strongly in their ability to form dense monomolecular layers on anatase. "N3" dye molecules readily arrange in a dense ordered monolayer (0.57 molecules / nm^2 on (101); 0.63 molecules / nm^2 on (001)). This involves an alignment of N3 molecules along <-1 1 1> on the (101) surface and along the <1 1 0> or <1 – 1 0>

diagonals on the (001) surface. "Black dye" molecules however exhibit a tendency to agglomerate (see Fig. 1). It is experimentally known that the performance of DSSC cells employing this dye can be significantly enhanced by coabsorbents such as deoxycholic acid. This could be reproduced by MD simulations clarifying the effect of the coadsorbent on the bonding topology of the dye as well as on the total and dye surface coverage. The coadsorbent does not change the packing density of the dye in the monomolecular layer, but helps to insulate the TiO2 from th electrolyte and also reduced the fraction of dye molecules with T-S bonds.
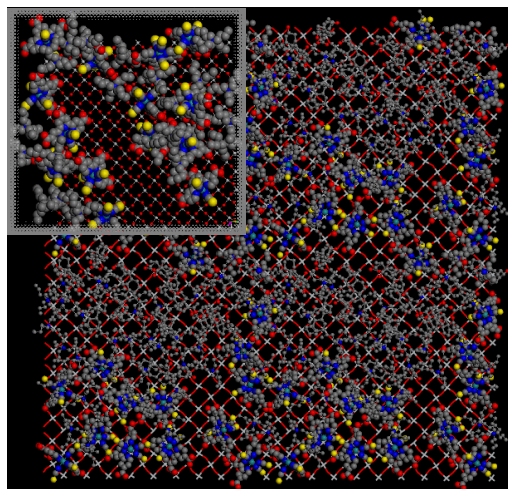

Fig. 1: Effect of deoxycholic acid on "black dye" molecule adsorprtion on a (001) anatase surface. Inset: Dye molecule agglomerates and uncovered surface regions in the absence of a coadsorbent.

References

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