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Adsorption of p-amino benzoic acid on anatase TiO₂ (101) - Supporting information.

UV-vis absorption onset.

In order to determine the absorption energy onset shift following adsorption of pABA on TiO₂ nanoparticles a suspension of TiO₂ nanoparticles (average diameter 20 nm, Sigma Aldrich) was prepared in deionized water. To this 500 mg of p-aminobenzoic acid was added. The resulting complex was removed from suspension by centrifugation and removal of the supernatant liquid. The complex was thoroughly rinsed with water and allowed to dry to a thick slurry. The slurry was spread onto a glass slide and UV-vis spectra recorded in reflection mode using an integrating sphere. A paste of TiO₂ nanoparticles was also prepared and UV-vis spectrum recorded, also in reflection mode. A clear absorption shift can be seen following adsorption of the p-aminobenzoic acid onto the TiO₂ nanoparticles. For the as-presented nanoparticles the onset is at 360 nm (3.4 eV), which is slightly larger than the bandgap of bulk anatase obtained from optical absorption measurements. Following adsorption of pABA the absorption onset begins at around 650 nm (1.9 eV) as can be seen in figure S1.

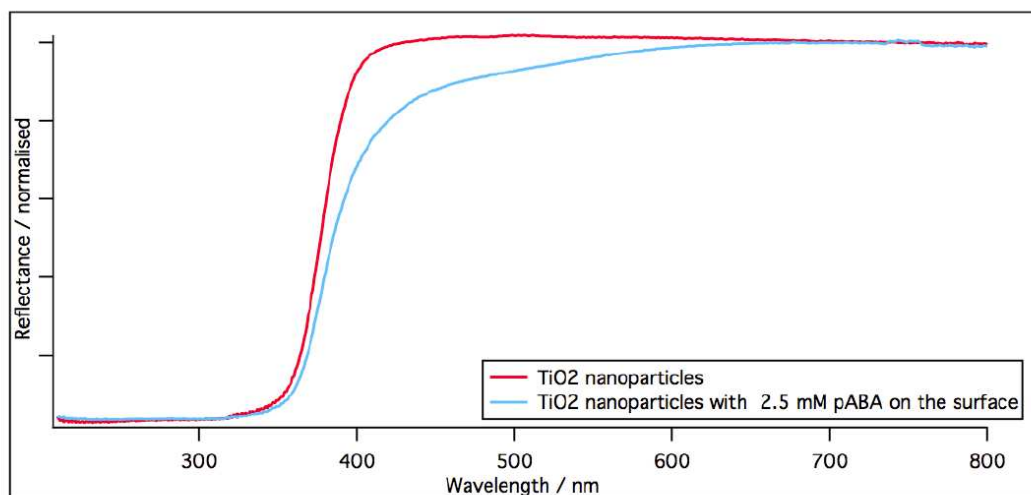


Figure S1. UV-vis spectra recorded in reflectance mode with an integrating sphere of TiO₂ nanoparticle paste (red line) and paste of pABA functionalized nanoparticles (blue line).

DFT Calculations – Bonding Mode and Orientation.

18 starting structures were investigated i.e.:

- (i) dissociative (bridging-bidentate) adsorption of the carboxylic group, both in a deprotonated molecule and in a zwitterion,
- (ii) molecular (non-dissociative) adsorption of the carboxylic group (2 starting structures),
- (iii) dissociative adsorption of the carboxylic group and adsorption of the amino group (2 starting structures with N bonded to Ti and 2 structures with H of the amino group hydrogen-bonded to surface O),
- (iv) molecular adsorption of the carboxylic group and adsorption of the amino group (8 starting structures with N bonded to Ti and 2 structures with H of the amino group hydrogen-bonded to surface O).

Of these only 13 optimized structures were obtained, because several starting structures resulted in the same molecularly-adsorbed final structure: for example, hydrogen bonding of NH_2 to the surface oxygen was always unstable, and the non-dissociated amino group bonded to Ti was also typically desorbed, leaving only the carboxylic (or carboxylate) group adsorbed.