

Adsorption Patterns of Caffeic Acid on Titania: Affinity, Charge Transfer, and Sunscreen Applications

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Titanium dioxide (TiO_2) is widely used as a white pigment in cosmetics, paints, papers and even some food products. Due to its light scattering properties, titanium dioxide is a common component of sunscreens along with other UV-protectors. Unfortunately, titanium dioxide-catalyzed photodegradation of many organic UV-protectors precludes utilization of natural and beneficial for skin photoprotectors such as caffeic acid (CA) in sunscreens containing titanium dioxide. The problem is mainly caused by the affinity of the catechol moiety of caffeic acid toward titanium dioxide that significantly accelerates photodegradation. We hypothesize that once the molecule of caffeic acid is adsorbed on titanium dioxide, the rate of its photodegradation is controlled by the efficiency of charge transfer in the excited state of the titanium dioxide-caffeic acid surface complex. The charge transfer at the titanium dioxide surface may be also responsible for the skin photodamage by titanium dioxide. Therefore, our research is focused on the tripartite objective: 1. Minimize adsorption of caffeic acid on titanium dioxide; 2. Minimize efficiency of the charge transfer in the photoexcited surface complexes between titanium dioxide and caffeic acid; 3. Measure photostability of caffeic acid in various titanium dioxide-containing compositions. We employed experimental study of adsorption isotherms of caffeic acid on different titanium dioxide polymorphs, computational evaluation of the adsorption energy and efficiency of charge transfer in the corresponding surface complexes, and finally, experimental assessment of photostability of titanium dioxide-caffeic acid composition using a solar simulator. We studied photodegradation of CA by TiO_2 nanoparticles with different additives suspended in an aqueous solution. Along those lines, we studied the relationship between morphology of titanium dioxide nanoparticles and their affinity to organic molecules (such as salicylic and caffeic acid) using multiple adsorption isotherms (such as Langmuir, Freundlich). We have computationally explored different modes of adsorption of CA on the surface of an anatase TiO_2 nanorod in terms of the binding energy, density of states, and other properties by density functional theory with PBE and HSE06 functionals, in the basis of plane waves, using VASP software.¹ The results reflect quantum confinement of TiO_2 nanorods.² Exploration of bright optical transitions, their oscillator strength, and corresponding pairs of Kohn-Sham orbitals reveal two channels for photoexcitations: (I) local excitation at either nanorod $\text{TiO}_2 + \hbar\nu \rightarrow \text{TiO}_2^*$ or adsorbate $\text{CA} + \hbar\nu \rightarrow \text{CA}^*$ or (II) photoinduced electron transfer from CA to titanium dioxide components $\text{TiO}_2 + \text{CA} + \hbar\nu \rightarrow \text{TiO}_2^- + \text{CA}^+$, in agreement with photophysics of similar adsorbates.³ We explore trends of charge transfer state formation through non-adiabatic relaxation events in comparison to quantum dynamics of electrons at similar interfaces of catechol dye and rutile surface⁴ and cyaniding dye and anatase nanowire.⁵ The information obtained from our computational study provides further understanding of the adsorption of catechol groups on the surface of titanium dioxide nanorod that will help us design titanium dioxide-based materials least damaging to CA and skin. Finally, we have shown experimentally that photostability of CA in the presence of titanium dioxide can be controlled by titanium dioxide morphology and significantly increased by the phosphate-ions competing with CA for the adsorption on titanium dioxide.

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