



Charge-transfer complex formation between TiO₂ nanoparticles and thiosalicylic acid: A comprehensive experimental and DFT study



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ABSTRACT

Under normal conditions, titanium dioxide does not absorb visible light photons due to large band gap. Nevertheless, when titanium dioxide nanoparticles (TiO₂ NPs) are surface-modified with thiosalicylic acid (TSA), their optical properties are altered owing to the formation of charge transfer complex that initiates absorption in the visible spectral range. Colloidal and sol-gel techniques were used to synthesize uniform TiO₂ NPs of different sizes (average diameters in the range 4–15 nm), and effects of their subsequent modification by TSA molecules were compared with effect of modification of commercial Degussa TiO₂ powder. Thorough microstructural characterization of TiO₂ nanoparticulates was performed including transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis, as well as nitrogen adsorption-desorption isotherms. Optical measurements revealed that all surface-modified TiO₂ samples with TSA have similar spectral features independent of their morphological differences, and, more importantly, absorption onset of modified TiO₂ samples was found to be red-shifted by 1.0 eV compared to the unmodified ones. The mode of binding between TSA and surface Ti atoms was analyzed by infrared spectroscopy. Finally, the quantum chemical calculations, based on density functional theory, were performed to support optical characterization of surface-modified TiO₂ with TSA.

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1. Introduction

Surface modification of TiO₂ with organic and organometallic molecules is primarily motivated by the application of these materials in photocatalysis [1–3] and photovoltaics [4,5]. Recently, a new approach for creating and utilizing bioinorganic composites of nanoscale TiO₂ has been extensively investigated for biomedical applications [6]. However, due to its large band gap [7], TiO₂ absorbs less than 5% of the available solar light photons. Therefore, sensitization of TiO₂ crystals and nanoparticles with appropriately chosen molecules can induce a significant red shift of their absorption threshold from the UV to the visible, thus improving the absorption of the solar spectrum as well as the efficiency of

photocatalytic and photovoltaic devices, notably dye-sensitized solar cells. Two distinct mechanisms of the charge injection from the adsorbate to the semiconductor, classified as Type I (straddling) and Type II (staggered), can be recognized. In Type I, a two-step process, the electrons from dye molecules, with the ground state located outside the semiconductor band gap, are first photoexcited to a dye excited state, followed by an electron transfer to the semiconductor conduction band [4,8]. Type II is a direct electron transfer in which the electron injection occurs in one step from the dye ground state with energy located in the semiconductor band gap to the semiconductor conduction band [9–11].

Over the last two decades, the surface modification of commercial TiO₂ (Degussa P25) with benzene derivatives (catechol and salicylic acid) was extensively studied [12–27]. However, colloidal TiO₂ NPs are unique compared to the bulk because of their larger surface area and the existence of surface sites with distorted

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coordination. Due to a large curvature of TiO₂ particles on the nanosize scale, formation of under-coordinated surface structure with square pyramidal geometry instead of octahedral takes place [28,29]. Consequently, surface Ti atoms are highly reactive and their binding to electron-donating ligands simultaneously adjusts their coordination to octahedral geometry and changes the electronic properties of TiO₂. In such hybrid structures, localized orbitals of surface-attached ligands are electronically coupled with the delocalized electron levels from the conduction band of a TiO₂ semiconductor [30]. As a consequence, absorption of light by the charge transfer complex (CTC) leads to the excitation of electrons from the chelating ligand directly into the conduction band of TiO₂ nanocrystallites (Type II). Thus far, the CTC formation accompanied with a red shift of the absorption onset by up to 1.3 eV has been primarily reported for colloidal TiO₂ NPs surface-modified with either catecholate- or salicylate-type of ligands [6,31–36]. Recently, Fujisawa et al. [37,38] reported the CTC formation between surface Ti atoms and π -conjugated mono-hydroxy compounds, as well as benzenedithiol compounds. For many applications, however, it is advantageous to use TiO₂ in powder form. Several studies have reported CTC formation between either catecholate- or salicylate-types of ligands with different TiO₂ in powder form: submicronic TiO₂ spheres [39,40], mesoporous nanopowders and commercial Degussa P25 [41], as well as commercial sodium trititanate (Na₂Ti₃O₇) nanotubes [42].

On the theoretical side, the quantum chemical calculations based on density functional theory (DFT) have been used to predict optical properties of inorganic/organic hybrids [33–37,43–46]. The agreement between calculated HOMO-LUMO gap values, as well as calculated electronic excitation and vibrational spectra, and the experimental data depends how well the chosen model mimics the corresponding system, and, of course, on the level of theory.

In this study, the size-effect of TiO₂ particles with under-coordinated surface structure on the CTC formation was evaluated and compared with commercial Degussa P25 TiO₂ powder. In addition, new type of ligand, biologically active thiosalicylic acid (TSA) molecule, with adjacent thiol and carboxyl groups, was introduced. Colloidal and sol-gel synthetic routes were used to prepare series of different in size TiO₂ NPs with narrow particle size distribution. Thorough microstructural characterization of synthesized TiO₂ samples, performed by transmission electron microscopy (TEM), X-ray diffraction (XRD) analysis, and nitrogen adsorption-desorption isotherms, were used to prove that TiO₂ samples have distinct particle sizes in the range from 4 to 15 nm. Special attention was paid to the comparison of optical properties of surface-modified TiO₂ NPs including Degussa P25 powder. Also, composition and stability constant of CTC were determined, while coordination of TSA to surface Ti atoms was studied using infrared spectroscopy. In addition, quantum chemical DFT calculations were used to calculate HOMO-LUMO gaps of CTC for TSA ligand attached to the surface of TiO₂ in the different coordination and compare them with experimental ones.

2. Experimental

2.1. Synthesis and characterization of nanostructured TiO₂

Colloids consisting of similar in size TiO₂ NPs were prepared either by hydrolysis of titanium isopropoxide (Ti(OCH(CH₃)₂)₄) or hydrolysis of titanium(IV) chloride (TiCl₄) as described elsewhere [47,48]. The concentrations of the TiO₂ colloids were determined from the concentration of the peroxide complex obtained after dissolving the colloid in the concentrated H₂SO₄ [49]. The undoped and doped mesoporous TiO₂ powders with Eu³⁺ ions were prepared following hydrolytic sol-gel route described in literature [50].

Detailed synthetic procedures for preparation of TiO₂ colloids and TiO₂ powders, as well as methodology of their characterization including TEM, X-ray diffraction (XRD) analysis and nitrogen adsorption-desorption isotherms is presented in [Supporting Information 1](#). Commercially available TiO₂ powder (Degussa P25) was used as received.

2.2. Surface modification of colloidal TiO₂ nanoparticles with TSA and determination of stability constants

Surface modification of colloidal TiO₂ NPs resulting in the formation of a CTC was accomplished by the addition of TSA up to concentrations needed to cover all surface sites ($[Ti_{surf}] = [TiO_2] \cdot 12.5/D$). Here, $[Ti_{surf}]$ is the molar concentration of surface Ti sites, $[TiO_2]$ is the molar concentration of TiO₂ in molecular units, and D is the diameter of the particle in angstroms [51]. In order to avoid precipitation or “gelling” of TiO₂ colloid, the pH of the stock colloidal solutions was adjusted in the range from 1 to 4, while ligand stock solutions were prepared in ethanol. For determination of CTC binding constants, the absorption spectra were recorded at room temperature using Thermo Scientific Evolution 600 UV-Vis spectrophotometer. In the application of continual variations method (Job's method) [52] for the spectrophotometric determination of the complex composition, the solutions were prepared by mixing different volumes of equimolar solutions of Ti_{surf} and TSA (6.4 mM). In this way, a series of solutions is prepared in which the sum of the total concentration of Ti_{surf} and modifier is constant, but their proportions are continuously varied: volumes of TiO₂ solution used varied from 1 to 9 ml and those of modifiers' solutions from 9 to 1 ml, with the total volume fixed at 10 ml.

2.3. Surface modification and optical characterization of nanostructured TiO₂ powders with TSA

Surface modification of TiO₂ powder obtained from colloid, as well as mesoporous TiO₂ powders synthesized by sol-gel route and commercial Degussa P25 TiO₂ powder, was performed by dispersing 0.1 g of powder in 10 ml of water containing 30.8 mg of TSA; molar ratio between any of the TiO₂ powders and ligand was fixed at 6.25:1. Formation of CTC was indicated by immediate coloration of dispersion. The mixture was left overnight and surface-modified TiO₂ powders were separated by centrifugation, washed several times with water/ethanol mixture in order to remove excess ligands, and finally dried at 40 °C in the vacuum oven for 24 h.

Optical properties of TiO₂ powders, as well as surface-modified TiO₂ powders with TSA were studied in UV-Vis spectral range by using diffuse reflectance measurements (Thermo Evolution 600 spectrophotometer equipped with Labsphere RSA-PE-19). Diffuse reflectance infrared spectra (DRIFTS) of TiO₂ powders, TSA, as well as surface modified TiO₂ powders with TSA were carried out using a Thermo Nicolet 6700 FTIR spectrometer with a Collector II Diffuse Reflectance Accessory at spectral resolution of 8 cm⁻¹ in the region of 4000–400 cm⁻¹.

2.4. Numerical calculation

All DFT calculations were carried out with the Gaussian 09 program package [53]. To investigate the electronic structure and optical properties of CTC, formed upon the adsorption of TSA on the TiO₂ surface, the hexa-cluster (TiO₂)₆ was used as a model system for calculations, its geometry taken from the existing literature, as shown in [Fig. 9](#) [54]. The ground-state geometry optimization of three different geometries of the TSA/H₂(TiO₂)₆ complex was performed at a gas phase by using HSE06 range-separated hybrid

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