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INVESTIGATION OF TiO₂ NANOPARTICLES WITH XAS AND SCATTERING (SANS AND SAXS) TECHNIQUES

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Abstract:

A variety of diagnostic techniques were used in order to understand the unique nature of 45 Å TiO₂ nanoparticles. Compared to bulk material, a shorter Ti-O bond distance and a decrease of the coordination number of surface Ti sites were found using XAS. IR spectroscopy suggests that upon surface modification with α mercaptocarboxylic acids surface Ti(IV) atoms become coordinated with five-membered ring formation to reestablish octahedral coordination. This results in the formation of a charge transfer complex with an optical absorption threshold at 520 nm. A rod-like, two-dimensional self-assembly of thiolactate modified 45 Å TiO₂ nanoclusters in water was detected by small angle neutron scattering (SANS).

Introduction:

Semiconductor assisted photocatalysis that is based primarily on TiO₂ has proven to be a promising technology for a variety of applications such as removal of organic and inorganic pollutants, metal ion reduction, or chemical syntheses.¹ Remediation of heavy metal ions such as Hg, Pt, Ag, Au, Cu, Rh, and Cr in a selective photoreductive degradation process results in the formation of the metals in very pure form making them available for recycling and reuse in other applications.

Surface modification of titanium dioxide nanoparticles can result in the enhanced kinetic and redox characteristics of this semiconductor.² Such particles can be advantageous for environmental remediation and photochemical energy conversion, in general. Nanoparticles that are in the intermediate size region (20-100 Å) exhibit hybrid properties between molecular ions and flat surfaces. Because of the large effective masses of electrons and holes, the electronic structure of nanoparticle TiO₂ does not change significantly relative to bulk TiO₂.³ However, due to the large surface to bulk ratio and their large curvature, nanoparticles can have a unique surface structure.

Experimental:

Colloidal TiO₂ was prepared by dropwise addition of titanium(IV) chloride to cooled water. The temperature and rate of component mixing of reactants were controlled by an apparatus developed for automatic colloid preparation.² Neutron scattering was measured for TiO₂ colloids dispersed in D₂O at the Small Angle Diffractometer, Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory.⁴ X-ray Absorption Spectroscopy (XAS) was performed at beamlines X6B, X18B and X19A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.⁵ EPR and IR were carried out on the Varian E-9 EPR (0.5 Gauss resolution, sensitivity 10⁻⁹M paramagnetic centers) and Nicolet 510 FTIR (4 cm⁻¹ resolution, sensitivity 0.002 a.u.).²

Results and Discussion:

In order to correlate the surface structure and the origin of the unique functions previously found in photocatalysis on nanoparticulate TiO₂,² we have investigated the effect of particle size on the coordination of surface Ti atoms using Ti K-edge X-ray Absorption Fine Structure (XAFS). As the particles become

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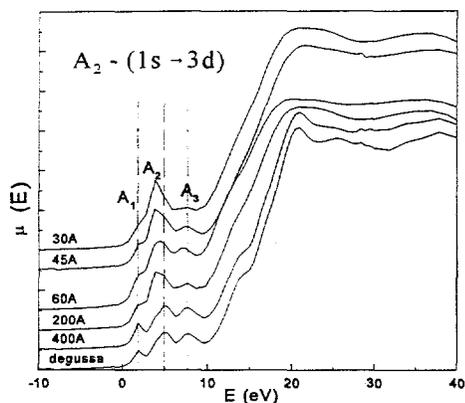
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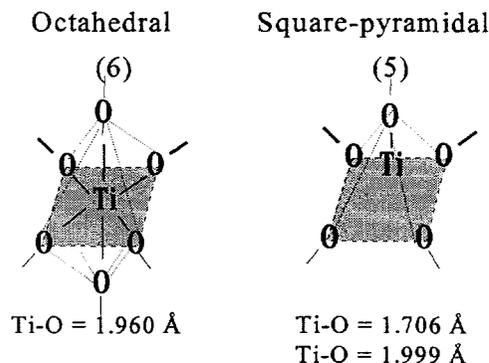
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smaller than 200 Å, the XAFS spectra reveal a shorter Ti-O bond distance and a change in the coordination number.⁵ This change is consistent with the adjustment of the coordination environment of Ti surface sites from sixfold-coordinated (octahedral) into fivefold-coordinated (square-pyramidal) followed by compression of a Ti-O bond.⁶ These results indicate a qualitative change of the surface with an increasing number of corner defects. These defects are much more reactive than the surface bonds at flat surfaces and tend to strongly bind ions either from solvent molecules or co-solutes. When strong chemical bonding is present, delocalization of the valence electrons can be extensive and provides a means to alter physical or chemical properties of the material.



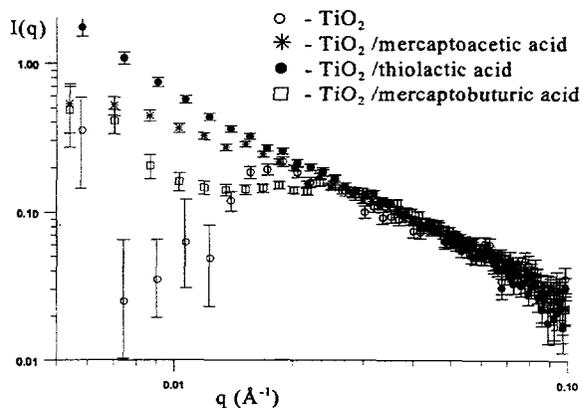
Pre-edge and XANES spectra of TiO_2 with different particle sizes at Ti K-edge ($E= 4.966$ KeV)



Schematic presentation of the coordination environment in flat surface and small particle ($D < 200$ Å) colloids.

Surface complexation of colloidal titanium dioxide nanoparticles (45 Å) by α mercapto substituted carboxylic acids results in the formation of a charge transfer complex with red shifted optical absorption that provides improved optical properties for solar energy conversion. The modification of large particle colloids (320 Å) does not lead to the formation of a charge transfer complex. The primary structure of these systems was determined by FTIR spectroscopy. It was found that α mercapto substituted carboxylic acids form a layer of bidentate bonded modifiers on 45 Å TiO_2 nanoclusters (with formation of five-membered rings around surface Ti atoms); while on large particle colloids they bind unidentate.

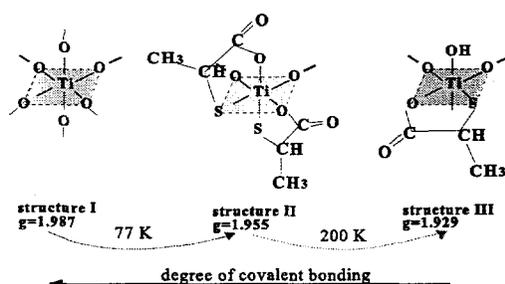
Using small angle neutron scattering (SANS) we found that surface modification with thiolactic acid (TLA) leads to self organization of 45 Å TiO_2 particles into long rods with the diameter the size of the particles (secondary structure). The diameter of the rods was identified to be 43.2 ± 1.6 Å, the same as the diameter of the particle determined using TEM. The diameter of the particle calculated from the molecular weight per unit length of the rods was found to be 40 Å. The slight underestimation of the mass was explained by difficulties in the determination of the partial specific volume of TiO_2



Effect of surface modifier on secondary structure determined by SANS.

particles covered with the layer of surface modifiers. Modification with mercapto acidic acid (absence of alkane group in α position) results in the formation of shorter rods with the same diameter, and shifts the optical absorption threshold to higher energies relative to the absorption threshold of TLA modified colloids. The existence of a longer chain alkane group in the α position (mercaptobuturic acid) results in a less stable system, as observed by reestablishment, in time, of the repulsion between particles. In this system the disappearance, in time, of the charge transfer band was observed in the optical spectrum of surface modified colloids. The formation of rod-like structures was not observed when the mercapto group was blocked by a methyl group or was separated from the carboxyl group with an additional CH_2 group. The self organization of TiO_2 particles in rod-like structures was explained by the hydrophobic interactions of methyl groups appendant to the colloid surface. The rod formation could provide a system which can allow axial charge separation across the assembled nanoparticle wires.

Interfacial electron transfer in TiO_2 nanoparticle colloids (45 Å) occurs via surface Ti(IV) atoms which are coordinated with the solvent molecules; while interfacial hole transfer occurs via surface oxygen atoms covalently linked to the surface titanium.⁷ The energy levels of these surface traps are located in the middle-gap region.



Effect of surface modifier on the surface trapping sites.

Therefore, the redox potentials of photogenerated charges in nanoclusters are reduced relative to the potential of conduction and valence band charges. Photogenerated charge pairs in nanoparticle TiO_2 colloids become trapped on the same particle. They are not physically separated to prevent rapid recombination of charges, unless very fast reactions with adsorbed species occur.⁸ Considering that sequential electron transfer is an essential feature of efficient photo-initiated charge separation, and the unique surface chemistry of nano-particles, we have modified the surface of nanoparticle colloids with different polydentate ligands.

EPR spectroscopy shows that illumination of these surface modified TiO_2 particles results in the efficient spacial separation of photoinduced charges. In band gap excitation, photogenerated holes are transferred to the derivatives at 4.2 K, while photogenerated electrons are trapped on the TiO_2 particle. Three signals are observed for electron trapping sites and are explained by the presence of different coordinations of surface Ti atoms with different degrees of covalent bonding. The energy of the trapping site was found to be proportional to the degree of covalent bonding. In CT excitation, electrons are transferred directly from the modifier primarily to the conduction band of TiO_2 from which they are thermalized on both the lattice and surface trapping sites. As redox properties of variable valence metal ions can be changed in complexation, we have investigated the possibility that coordination of surface Ti atoms has the same effect on the redox potential of photogenerated carriers.

We have shown, using EPR spectroscopy, that surface modification of small particle colloids with α mercapto substituted carboxylic acids has a dramatic effect on the reducing properties of TiO_2 . Illumination of aqueous (D_2O) colloidal solutions of surface modified TiO_2 nanoclusters resulted in the formation of hydrogen (deuterium) atoms with the redox potential of $E^\circ(\text{H}^\bullet/\text{H}^+) = -2.1\text{V}$ vs. NHE, a slightly less powerful reducing species than hydrated electrons. All redox species with the redox potential more positive than -2.1V (such as Hg^{2+} , Pb^{2+} , Cd^{2+} , Ni^{2+} or Cu^{2+}) can be effectively reduced on surface modified TiO_2 nanoparticles. Thus, surface modification of TiO_2 nanoparticle colloids improves their reducing properties and results in

a photocatalyst capable of sequestering and removing highly toxic heavy metal ions from aqueous solutions by reducing them into their less toxic metallic form.

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