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on Fundamental and Applied Aspects of
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SURFACE MODIFICATION OF ANATASE NANOPARTICLES WITH SUBSTITUTED CATECHOLATE TYPE LIGANDS

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ABSTRACT

The surface modification of nanocrystalline TiO_2 particles (45 Å) with catecholate-type ligands having electron donating (4-methylcatechol, 4MetCat) and electron withdrawing (4-nitrocatechol, 4NitCat) substituent groups, was found to alter the optical properties of nanoparticles in a similar way to catechol (Cat). The formation of the inner-sphere charge-transfer (CT) complexes results in a red shift of the semiconductor absorption onset compared to unmodified nanocrystallites, being slightly less pronounced in the case of electron withdrawing substituent. The investigated ligands have the optimal geometry for binding to surface Ti atoms, resulting in ring coordination complexes of catecholate type (binuclear bidentate binding - bridging) thus restoring six-coordinated octahedral geometry of surface Ti atoms. The binding structures were investigated by using FTIR spectroscopy.

INTRODUCTION

Widespread interest in the modification of TiO_2 surfaces with organic and organometallic molecules is largely motivated by the application of these materials in photocatalysis and photovoltaics [1]. Due to its large band gap (E_g = 3.2 eV), TiO_2 absorbs less than 5% of the available solar light photons. Sensitization of TiO_2 crystals and nanoparticles with appropriately chosen molecules can indeed lead to 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. Owing to the large curvature of TiO_2 particles on the nanosize scale, the surface reconstructs in such a manner that distorts the crystalline environment of surface Ti atoms forming coordinatively unsaturated Ti atoms which are very reactive. Absorption of light by the CT complexes formed upon adsorption of modifier ligands onto TiO_2 yields to the excitation of electrons from the chelating ligand directly into the conduction band of TiO_2 nanocrystallites (DSSC Type II). This results in a red shift of the semiconductor absorption compared to that of unmodified nanocrystallites and enables efficient harvesting of solar photons.

EXPERIMENTAL

The colloidal TiO_2 dispersions were prepared by the dropwise addition of $TiCl_4$ to cooled water [2]. Surface modification of TiO_2, in methanol/water=90/10 solutions at pH 2, resulting in the formation of CT complexes was achieved by the addition of surface-active ligands up to concentrations required to cover all surface sites. For the determination of CT complex binding constants the absorption spectra were recorded at room temperature using a Thermo Scientific Evolution 600 UV/Vis spectrophotometer. The stoichiometric ratio between Ti_{surf} atoms and modifiers in the CT complexes was checked by Job's method of continuous variation. Infrared spectra were recorded in attenuated total reflection (ATR) mode using a Nicolet 380 FTIR spectrometer equipped with a Smart Orbit^{TM} ATR attachment containing a single reflection diamond crystal.

RESULTS AND DISCUSSION

When TiO_2 particles are on the nanosize scale, a large fraction of the atoms that constitute the nanoparticle is located on the surface, with significantly altered electrochemical properties. Among them, the existing undercoorinated (pentacoordinated, square pyramidal) defect sites are the source of novel, enhanced and selective reactivity of nanoparticles toward bidentate ligand binding. Upon binding, the new hybrid properties arise from the ligand-to-metal CT interaction due to orbital mixing between the molecular orbitals of the ligands and the conduction band orbitals of the nanoparticles. The CT complex formed leads to a shift in the effective band gap of the material to a lower energy i.e. the onset of the absorption of these CT nanocrystallites is red shifted when compared to unmodified TiO_2.

By extracting the corresponding onset energies from the absorption spectra of surface modified TiO_2 nanoparticles (Fig 1), the effective band gap energies ($E = hc/\lambda$) of Cat, 4MetCat and 4NitCat modified TiO_2 nanoparticles were calculated to be 2.1, 2.1 and 2.3 eV, respectively. From the absorption measurements (Benesi-Hildebrand plot), the stability constants were determined to be: 3200 M^{-1} for Cat, 3200 M^{-1} for 4MetCat and 2400 M^{-1} for 4NitCat. Job's plots confirmed that the molar ratio between Ti_{surf} atoms and ligands in the complex is 2:1.

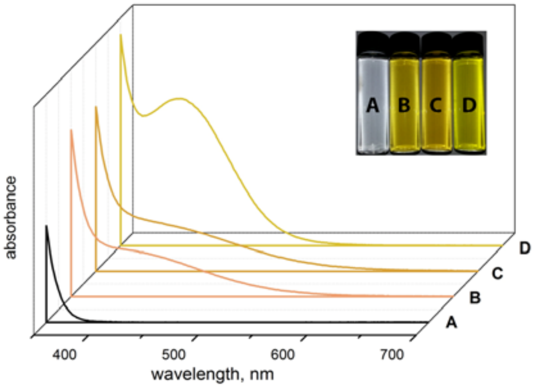

Figure 1. Absorption spectra of surface modified TiO_2: A) bare TiO_2; B) Cat; C) 4MetCat; D) 4NitCat

The ATR-FTIR spectra of Cat, 4MetCat and 4NitCat, free and adsorbed on TiO_2 nanoparticles are presented in Fig. 2. The main bands and their assignments [2, 3] in free modifiers (Fig. 2, upper curves) are as follows: first two bands from the left are bending δ(CH) vibrations, followed by bending vibrations of the phenolic group δ(OH) in the 1150 - 1450 cm^{-1} region coupled with the stretching vibrations of the phenolic group ν(CO) in the 1200 - 1300 cm^{-1} region. The stretching vibrations of the aromatic ring ν(C=C) are in the 1450 - 1650 cm^{-1} region. Substituent groups also contribute to the above presented vibration bands: δ(CH) vibrations in the methyl group of 4MetCat are coupled to all bands in the 1000 – 1450 cm^{-1} region, while in the case of 4NitCat additional vibrations are coupled: ν(CN) at 1079, 1120 and 1327 cm^{-1}, ν $(NO_2)^{sym}$ at 1327 cm^{-1} and $\nu(NO_2)^{asym}$ at 1592 and 1628 cm^{-1}. Upon adsorption of catecholate-type ligands onto TiO_2 (Fig. 2, lower curves) the difference between FTIR spectra of free and adsorbed modifiers appears, being most pronounced in the 1000 – 1450 cm^{-1} region, indicating surface complexation with phenolic groups bound to the oxide surface in bidentate form [2]. Bands around 1100 cm^{-1} and in the 1240-1300 cm^{-1} region, could be assigned quite confidently to aryl-oxygen-Ti stretching vibrations ν(C-O-Ti) [4]. The binding of modifiers to TiO_2 via two adjacent phenolic groups even affects the stretching of the aromatic ring ν(C=C) and the nitro group $\nu(NO_2)$ moving them to the lower wavenumbers.

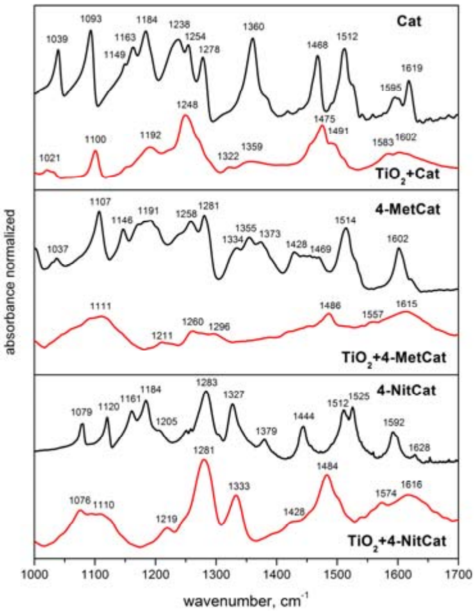

Figure 2. FTIR spectra of free ligands (upper curves) and adsorbed on TiO_2 (lower curves)

CONCLUSION

All investigated ligands (Cat, 4MetCat and 4NitCat) form inner-sphere charge-transfer complexes with TiO_2 nanoparticles (d = 45 Å). The binding of the modifier molecules to undercoordinated surface Ti atoms (defect sites) results in a significant shift in the onset of absorption to the visible spectral range. Both substituted modifiers decrease the effective band gap energy of surface modified TiO_2 i.e. less energy is needed to inject an electron into the conduction band of TiO_2 nanoparticles, the effect being less pronounced in the case of electron-withdrawing group. From the Benesi-Hildebrand plot, the stability constants at pH 2 of the order 10^3 M^{-1} have been determined. The binding structures were investigated by FTIR spectroscopy. According to Job's method of continuous variation binding was found to be through bidentate binuclear (bridging) complexes.

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