Surface Modification of TiO₂: Correlation between Structure, Charge Separation and Reduction Properties†

Marion C. Thurnauer, Tijana Rajh and David M. Tiede

Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439 USA

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Surface complexation of colloidal titanium dioxide nanoparticles (40 Å, anatase structure) by α-mercapto-substituted carboxylic acids results in the formation of a charge transfer complex with an optical absorption threshold at 520 nm. It was found by EPR spectroscopy that illumination of these surface-modified TiO₂ particles, which leads to the charge transfer complex and/or band gap excitation, results in the efficient spatial separation of photoinduced charges. Photogenerated holes are transferred to the derivatives at 4.2 K, while photogenerated electrons are trapped on the TiO₂ particle. Visible excitation (400 nm cut-off filter) results in localization of photogenerated holes on the carboxy group, while UV excitation results in localization on the most distant hydrocarbon group of the derivative. Both band gap and CT excitation of TiO₂ lead to the reduction of Pb^{2+} ions to metallic lead ($E° = -0.126$ V vs. NHE), while only band gap excitation leads to the reduction of Cd^{2+} ions to its metallic form ($E° = -0.405$ V). The EPR signal for trapped electrons disappeared as a result of the reduction of Pb^{2+} or Cd^{2+} ions, and metallic lead was observed to precipitate.

Numerous studies in the last several years have demonstrated the efficiency of photocatalytic oxidation of organic compounds in illuminated TiO₂ suspensions.[1] Because this oxidation process converts a broad range of organic compounds into CO_2, H_2O and simple mineral acids by photogenerated positive holes, it has the potential for application in the removal of organic contaminants from waste waters and drinking water supplies. To maintain neutrality, both photogenerated electrons as well as positive holes have to be consumed efficiently in redox processes on the semiconductor surface. In previous studies, photogenerated electrons were consumed in the reaction with dissolved oxygen in order to achieve fast oxidation of organic compounds. However, organic pollutants are often accompanied by heavy metal ion contaminants that can be reduced by photogenerated electrons into their less toxic, insoluble metallic form.

Photoreduction of divalent metal ions is a two electron transfer process. Usually, the first electron transfer process requires very negative potentials that cannot be achieved with conduction band electrons from TiO₂. The reduction of divalent metal ions to their metallic form can occur only if there is an accumulation of electrons that can be simultaneously injected into the surrounding liquid containing metal ions. The reduction of metal ions that occurs at the two-electron transfer potentials are generally much less negative with respect to the potentials for one-electron transfer processes. However, it has been shown recently that the Fermi level of small metallic particles is still significantly more negative than the one reported for electrochemical potential. For example, 50 Å lead particles are reported[2] to have a potential of ~ -0.44 V* although a corresponding electrochemical potential is -0.126 V. Thus, it can be expected that the metal deposition potential in nanocrystalline TiO₂, which results in the formation of nanosize metallic clusters on a TiO₂ support, will be more negative than corresponding electrochemical values and more positive than one electron transfer potentials observed in homogeneous solutions.

Illumination of TiO₂ with light energy greater than the band gap (3.2 eV) generates electron hole pairs that can migrate to the surface of the particle and participate in reduction and oxidation processes. Theoretically, all

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* All potentials given in this paper are referred to the normal hydrogen electrode.

the solution species that have a reduction potential more positive than photogenerated electrons (-0.26 V at pH 3.5) and an oxidation potential more negative than photogenerated holes (2.94 V at pH 3.5) can be reduced and oxidized on illuminated TiO_2 surfaces, respectively. Due to the short lifetime of charge carriers, one or both charge carriers formed during illumination have to be removed from the particle before their recombination. This situation can be obtained only in the fast reaction with adsorbed species. If the particle size of TiO_2 is significantly decreased to the nanometer size regime, large surface areas can be obtained. This would result in higher adsorption rates and consequently in a higher efficiency of photocatalytic reactions. However, in the small particle colloids the large fraction of surface atoms are coordinated with solvent molecules which act as trapping sites for photogenerated charges. As a result of charge trapping, the redox properties of photogenerated charges are reduced relative to the conduction and valence band charges.

Recently, we have shown that surface modification of TiO_2 with cysteine results in the enhanced rates of lead photoreduction due to the change in redox properties of the semiconductor and increased adsorption of metal ions after surface modification.[3] We have shown that strong adsorption of electron-donating redox couples shifts the bands to the negative potentials leading to the enhanced reduction properties of TiO_2. In this work we report surface modifications with bidentate mercapto-carboxylic acids which result in the enhanced reducing properties of TiO_2 so that reduction of cadmium ions to metallic cadmium was observed $[E^\circ(Cd^{2+}/Cd) = -0.405$ V]. The structures of surface modifiers on the TiO_2 surface and their electrochemical properties were correlated with the charge separation distances and reduction abilities obtained after illumination of surface modified colloids.

Experimental

All the chemicals were reagent grade and used without further purification (Aldrich or Baker). Triply distilled water was used. The pH was adjusted to pH 3.5 with NaOH or HCl. Oxygen was removed by bubbling with argon or nitrogen.

Colloidal TiO_2 was prepared by the 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.[3] A multi-port adjustable-temperature liquid nitrogen cooled gas flow system was used to control the temperature of $TiCl_4$ prior to addition to water and control the temperature of the reaction vessel. A peristaltic pump with variable size outlet ports was used to control the drop size as well as the drop rate of $TiCl_4$. Following $TiCl_4$ hydrolysis, the solution was dialyzed against distilled water at 4 °C. The concentration of TiO_2 (0.1–0.6 M) was determined from the concentra-

tion of the peroxide complex obtained after dissolving the colloid in concentrated H_2SO_4.[4] The particle size and structure were determined by TEM to be 40 Å and anatase structure, respectively.

Apparatus. EPR: samples were excited at 77 K by a Questek 2400 excimer laser (308 nm, 150 mJ/pulse; 3000 pulses). After laser irradiation, the samples were transferred to a variable temperature Dewar mounted in the EPR spectrometer (Varian E-9). Samples were checked for background EPR signals before irradiation. The g-factors were calibrated by comparison with an Mn^{2+} standard in SrO matrix ($g = 2.0012 \pm 0.0002$).[5] Lead ions were added as $Pb(CH_3COO)_2$.

FTIR: measurements were performed on a Nicolet 510 Fourier transform infra-red spectrometer equipped with a Spectra-Tech, Inc. diffuse reflectance accessory. The resolution was 4 cm^{-1}. All samples were 8% wt of sample in KBr matrix. Typically 100 scans were performed for each spectrum. All results are presented as normalized Kubelka–Munk plots. Lead ions were added as $Pb(NO_3)_2$.

Cyclic voltammetry: glassy carbon was used as the working and SCE as the reference electrode, 10^{-2} M KCl was the supporting electrolyte, and Ar was bubbled before and during the scans. The potentials were scanned from 0 to 1.8 V and from 0 to -1.4 V and back.

UV–VIS absorption spectra were recorded on a Shimadzu MPS-2000 instrument. A 300 W Xe lamp (Orion Corp) was employed for steady-state illumination.

Results and discussion

Our approach for the performance improvement of TiO_2 photocatalyst for photocatalytic reduction of heavy metal ions is to use multifunctional ligands which bind both the colloid surface and heavy metal ions. The surface of colloidal TiO_2 was modified with a series of bidentate and tridentate compounds that have the mercapto, carboxy and amino groups in different relative positions and different hydrocarbon chain lengths. The structural, dynamic and redox potentials of surface modified colloids were investigated by using IR spectroscopy, EPR spectroscopy and cyclic voltammetry, respectively.

Characterization of the surface structure of modified TiO_2. It is known that surface hydroxy groups of titanium dioxide are the origin of the acidic or basic properties of these solids. When H^+ in an OH group is substituted with an adsorbed molecule, the OH group shows protonic acidity (metal ions,[6] amines,[7] etc.). OH groups can also behave as Lewis-type acid sites in the complexes when an OH group coordinates basic compounds (ammonia, pyridine, etc.), or have basic characters in contact with CO_2 or acids (p$K < 6.5$) where the OH group is replaced with adsorbate.

The infrared spectrum (4000–1000 cm^{-1}) of colloidal TiO_2 consists of two absorption bands: a broad absorp-
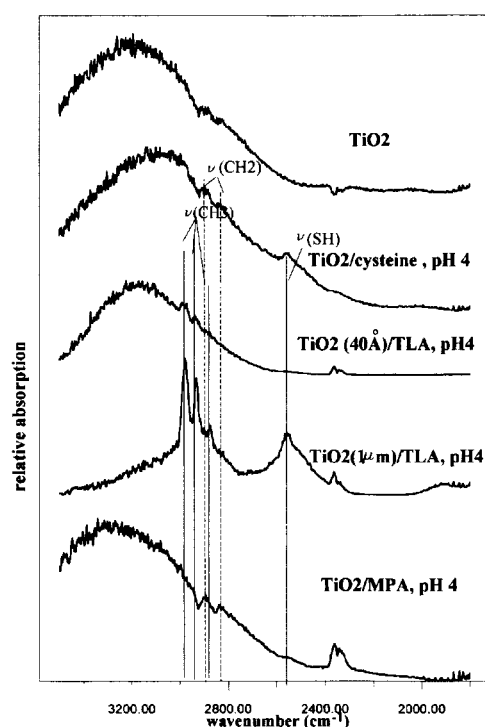
Fig. 1. Adsorption of surface modifiers on TiO_2 colloids. Infrared spectra in the region $1800–4000$ cm^{-1} of dried samples of (from the top) TiO_2 (40 Å); 0.1 M cysteine modified 0.3 M TiO_2 (40 Å); 0.1 M thiolactic acid on TiO_2 powder ~ 1 μm particle size thoroughly washed with CH_3OH; 2×10^{-2} M thiolactic acid modified 0.3 M TiO_2 colloids (40 Å) thoroughly washed with CH_3OH; 0.1 M mercaptopropionic acid modified 0.3 M TiO_2 (40 Å). Normalization of the spectra was made assuming that the intensity of the bending vibration of the CH_3 group or the CH_2 group was not affected by adsorption.

Fig. 2. Adsorption of surface modifiers on TiO_2 colloids. Infrared spectra in the region $1000–1800$ cm^{-1}. All other parameters as in Fig. 1.

Scheme 1.

tion maximum ($3800–2600$ cm^{-1}) centered at 3200 cm^{-1} which is the characteristic frequency for a hydrogen-bonded OH stretching vibration[8] (Fig. 1), and a narrower band at 1620 cm^{-1} which is associated with the scissoring vibration of adsorbed water molecules[9] (Fig. 2). Addition of carboxylic acids results in the replacement of surface OH groups and coordination of surface Ti atoms with a carboxy group (Scheme 1).

Coordination at the surface of TiO_2 with particle diameter > 200 Å was observed for every bidentate ligand containing a carboxy group that was investigated (thiolactic acid, mercaptoacetic acid, mercaptopropionic acid, cysteine, S-methylcysteine and alanine). Due to the change in the energy of vibration of the carboxy group obtained by infrared spectroscopy of a dried colloid sample, we conclude that, at pH 4, the carboxy group of the surface modifier is involved in the binding to the TiO_2 surface [disappearance of v(C=O) and consequent appearance of v(COOM)].[3] In contrast, the stretching vibration of the SH group (~ 2550 cm^{-1}) was not affected by adsorption. Similar binding was shown for cysteine and S-methylcysteine modified 50 Å TiO_2 colloids demonstrating that the thiol group does not coordinate with
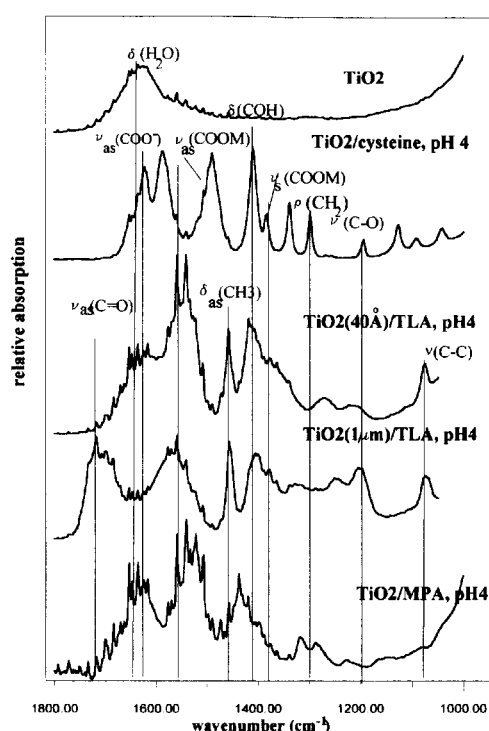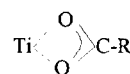
the TiO_2 surface. When semiconductor particles are in the nanometer size regime however, a large fraction of surface atoms are coordinated with OH groups and solvent molecules. A 40 Å particle TiO_2 has 40% of the titanium atoms located at the particle surface. Due to the large curvature of the particles, a significant number of surface atoms become 'corner dislocations' that have up to four bonds saturated with OH groups which can be replaced after surface modification. These defects are chemically very active and can form unusual complexes with solution species. It is known that titanium ions readily form complexes with oxygen atoms from various oxygen-containing groups, but they also form complexes with thiol alcohols, thioesters or thiocarbamides.[10]

When a 50 Å TiO_2 colloid was modified with thiolactic acid [$CH_3CH(SH)COOH$, TLA], a different coordination structure was found. FTIR spectra showed that the stretching vibration of SH (2550 cm^{-1}) disappeared. At the same time, the disappearance of the [C=O bond (1720 cm^{-1})] asymmetric vibration and the appearance of both asymmetric stretching vibration (1550 cm^{-1}) and symmetric stretching (1350 cm^{-1}) of polarized CO_2^- were detected (Fig. 2). This spectrum, in the range $1000–1800$ cm^{-1}, represents a typical spectrum of carboxylate species. The formation of carboxylate species,

together with loss of hydrogen from the SH group, indicates that both sulphur and oxygen are chelating
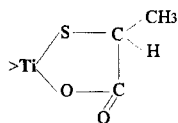
Scheme 2.

surface Ti^{IV} atoms (Scheme 2). This suggests that the chelate forms a five-membered ring that does not require distortion of bond angles or distances, and has a favorable angular configuration for octahedral coordination of Ti^{IV} surface atoms. The same changes in the infrared spectra are observed for mercaptoacetic acid.

We have found that this five-membered ring around surface Ti also affects the optical properties of TiO₂. Thiolactic acid forms a charge transfer complex with small particle TiO₂ that has an optical absorption threshold at 570 nm and a maximum at 380 nm (extinction coefficient for TLA 3.25×10^4 M^{-1} cm^{-1}, Fig. 3). From a Benesi–Hildebrandt plot a stability constant of 400 M^{-1} was determined and the concentration of the charge transfer complex was calculated to be 8.7×10^{-5} M. This compares with the particle concentration of a TiO₂ colloid of 9.1×10^{-5} M. This indicates that under our experimental conditions all particles contribute to charge transfer complex absorption.
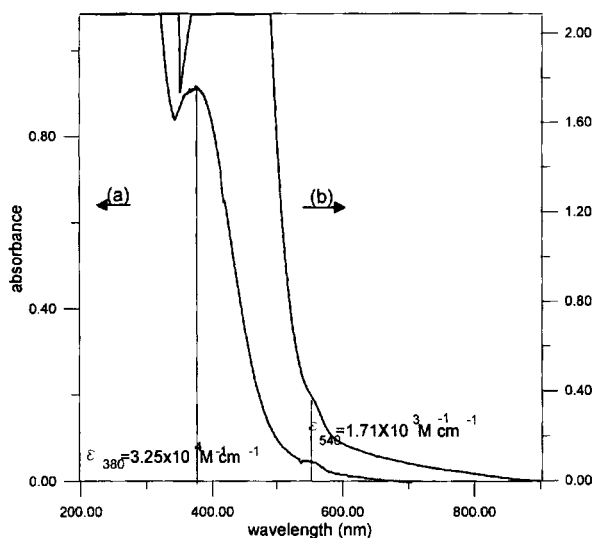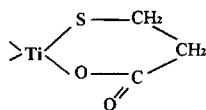

Fig. 3. Charge transfer complex between thiolactic acid and TiO₂ (40 Å) colloids. Absorption spectra of two different concentrations re-dispersed in methanol: (a) 1.42×10^{-4} M; (b) 1.46×10^{-3} M. Extinction coefficients were obtained from the intercept of a Benesi–Hildebrandt plot. Optical path length is 0.2 cm.

Scheme 3.

Adsorption of β-mercaptopropionic acid (MPA) on a TiO₂ colloid surface did not change the optical properties in the UV–VIS range of the spectrum. The spectra obtained in the IR region suggest that MPA also chelates surface Ti^{IV} through sulphur and oxygen atoms [Scheme 3, Figs. 1, 2, disappearance of v(SH) 2550 cm^{-1}, δ(CH₂-SH)wag, formation of v(CO₂$^-$) asym 1500 cm^{-1}, and v(CO₂$^-$)sym 1400 cm^{-1}]. The formation of the charge transfer band in the visible region of the spectrum was not observed in this case, probably as the result of the strained configuration in a six-membered chelate complex of MPA with surface Ti^{IV} atoms. However, addition of lead ions that bind to the other oxygen in the carboxy group of MPA modified TiO₂ resulted in sulphur desorption from the surface and the consequent appearance of a stretching vibration of the SH group at 2550 cm^{-1} in the IR spectrum suggesting the binding structure shown in Scheme 4.
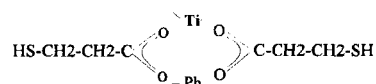
Scheme 4.

Charge separation in the surface modified TiO₂. We have found by IR spectroscopy that oxygens from the carboxy group of surface modifiers are covalently linked to the TiO₂ lattice. Thus, it might be expected that for cysteine and S-methylcysteine the carboxy group acts as the initial trapping site for photogenerated holes, followed by transfer of the holes within the surface modifier molecule. Indeed, after illumination of cysteine modified TiO₂ (Fig. 4) at low temperatures (4–77 K) the holes are trapped on cysteine as a carboxyl radical ($g_x = 2.022$ and $g_y = g_z = 2.004$), while the electrons are trapped on the TiO₂ particle. In cysteine modified TiO₂, formation of a sulphur-centered radical is observed at 150 K, so that the charge separation distance increases further with increasing temperatures. The increased separation distance prevents recombination of trapped charges and enhances the lifetime of trapped electrons. In the presence of lead ions the signal for trapped electrons disappears, indicating that trapped electrons react with lead ions reducing them to metallic lead. However, when interparticle charge transfer in the surface modifier is prevented by blocking the mercapto group that acts as the hole trap (S-methylcysteine), stabilization of charge separation is not achieved and precipitation of lead was much less effective.

In cysteine modified TiO₂ the mercapto group was found not to be bound to the TiO₂ surface, and this group acts as the most stable hole trapping site in this material. It is interesting to determine the nature of the hole and electron trapping sites when the mercapto groups are chelating Ti surface atoms. Illumination of TLA and MAA modified TiO₂ nanoparticles leads to the trapping of the holes also. At very low temperatures
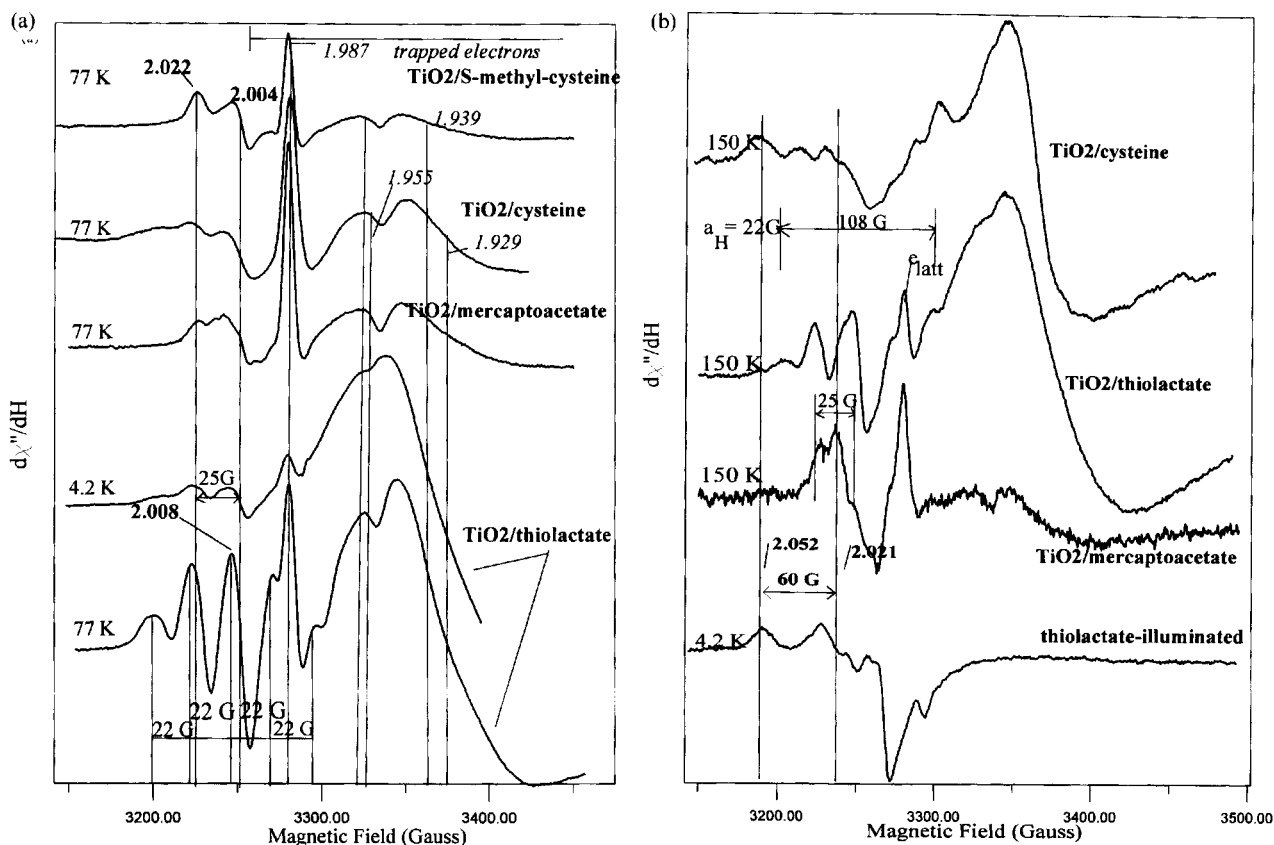
Fig. 4. Surface modification of 40 Å TiO$_2$ colloids with different mercapto-carboxylic acids. EPR (X-band) spectra of degassed aqueous TiO$_2$ colloids (0.3 M) irradiated with a 308 nm excimer laser (a) in the presence of 0.1 M S-methylcysteine, pH 4, illuminated at 77 K recorded at 8 K; 0.1 M cysteine, pH 4, recorded at 8 K; 2 × 10^{-2} M mercaptoacetic acid, pH 4, illuminated at 77 K recorded at 8 K; 2 × 10^{-2} M thiolactic acid, pH 4, illuminated and recorded at 4.2 K, and illuminated at 77 K and recorded at 8 K and (b) the spectra in (a) recorded at 150 K. At the bottom: illumination of thiolactic acid only, at 4.2 K leads to the formation of the sulphur-centred radical dimer of thiolactic acid.

(< 8 K) the EPR spectrum of trapped holes is composed of g factors 2.004, 2.022 and a broad shoulder at g = 2.035 (Fig. 4). The signals obtained at g factors 2.004 and 2.022 again correspond to the hole trapped at the carboxy group.
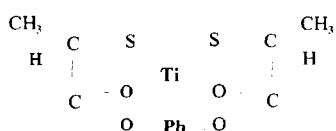
When the temperature is increased beyond 80 K further hole transfer occurs in TLA but not in MAA modified TiO$_2$. The EPR spectrum of TLA modified TiO$_2$ is now composed of five lines with a hyperfine coupling of a_H = 22 G. Because the signal for trapped electrons is still present indicating that electrons cannot be involved in the reduction of TLA, we attribute this radical to a ·CH$_2$CH radical,[11] the product of oxidation of TLA. The sulphur radical of TLA would have the EPR spectrum either at g ~ 2.17 in the RS· form or g_x = 2.052, g_y = 2.021 and g_z = 2.001 in the RS·-SR form,[12] none of which were observed upon illumination of surface modified TiO$_2$. These results show that once the mercapto group is bound to a metal it does not act as the trap for photogenerated holes. Instead, the hydrocarbon group in the α position becomes the oxidation center.

A five-line spectrum is observed in the temperature range 8–150 K above which the spectrum disappears and

a new spectrum showing trapped holes with g_x = 2.013, g_y = 1.976 and g_z = 1.907 appears. The intensity of the spectrum attributed to trapped electrons did not change after increasing the temperature. These results indicate that the hole primarily trapped near the particle surface moves away with increasing temperature to the CH$_3$ group. As the distance between charges is enhanced, charge separation becomes more efficient and more charges are available for reactions at the colloid surface. In the TLA-TiO$_2$ system, TLA acts as a sacrificial electron donating species, so that trapped electrons can be used for reduction of all the species having a potential more positive than trapped electrons. From these EPR measurements we expect two surface modifiers that have the hole traps that enhance charge separation to be effective for metal ion reduction: cysteine (mercapto group) and TLA (side hydrocarbon group).

Deposition of lead. Lead ions bind to carboxy-group containing surface modified TiO$_2$ colloids in a very specific manner. The main features of the IR spectra of these species are the appearance of two new bands at 2400 cm^{-1} and 1380 cm^{-1}. These bands were previously

reported only for strongly perturbed CO_2, linearly O-ended adsorbed on anatase[13] and assigned to the vibration of Ti–O–C–O stretching modes. The two C–O stretching modes should depend on the type of interaction (i.e., from electron density on C–O bonds and on O–C–O angles). We propose that after the addition of lead ions, the symmetrical vibration of the five-membered ring chelates has a high degree of coupling with the symmetrical stretching of the carboxy group, which in this way becomes enhanced compared with the asymmetrical stretching. Thus, disappearance of the asymmetrical stretching modes ($1500–1650\,cm^{-1}$) indicates formation of a symmetrically resonant group where the double bond character is lost and the carboxy group is resonating between surface Ti and Pb atoms. The carboxy group bridges Ti and Pb ions (Ti–O–C–O–Pb), and in this way Pb becomes linked to the particle surface, and becomes a continuation of the particle lattice (Schemes 4 and 5).

$$
\begin{array}{ccccc}
CH_3 & & & & CH_3 \\
\quad C & S & \quad & S & C \\
H & & & & H \\
\quad C & O & Ti & O & C \\
& O & Pb & O &
\end{array}
$$

Scheme 5.

Fig. 5. Deposition of metallic lead after illumination of thiolactate modified TiO₂. Absorption spectra of (a) 2×10^{-4} M thiolactate modified TiO₂ (0.2 M); (b) illuminated for 10 min with 300 W Xe-lamp. After illumination the absorption spectrum in the $\lambda > 500$ nm region resembles the spectrum of (c) electrons trapped on TiO₂ particles obtained after illumination of TiO₂ (0.2 M) in methanol; (d) after addition of 0.01 M Pb(ClO₄)₂ into (b) in the dark.

Electron donating properties of surface modifiers. All investigated multifunctional ligands are electron-donating compounds. It is a known fact that strong adsorption of electron donating compounds on electrodes can shift the flat band potential to negative values and therefore enhance reducing properties of electrodes.[14] We have shown that adsorption of TLA or cysteine leads to the enhanced reducing properties of TiO₂.[3] The flat band potential of TiO₂ (V_{fb}) which describes the potential of the electron at the TiO₂–liquid interface is given by[15] eqn. (1).

$$V_{fb} = -0.05 + (-0.059)\,pH \tag{1}$$

The reducing ability of the electrons in unmodified TiO₂ at pH 3 is -0.24 V. We have found that surface modified TiO₂ led to the accumulation of electrons in semiconductors that can reduce methylviologen. When TiO₂ was modified with TLA, all trapped electrons were converted into MV^{+}. Using $E(MV^{2+}/MV^{+}) = -0.443$ V, we estimate the reduction potential of surface modified TiO₂ to be more negative than -0.443 V. The potential of accumulated electrons exceeds the energy for precipitation of small lead clusters (given with their Fermi level < -0.443 V), and the precipitation of lead was observed upon addition in the dark of lead ions to a solution of TLA modified TiO₂ which had been illuminated and stored in the dark. The characteristic blue color of trapped electrons disappeared after the addition of lead ions, and the formation of a brown colloidal solution was observed (Fig. 5). In the case when lead ions were present during illumination, rapid formation of metallic lead was observed spectroscopically and complete
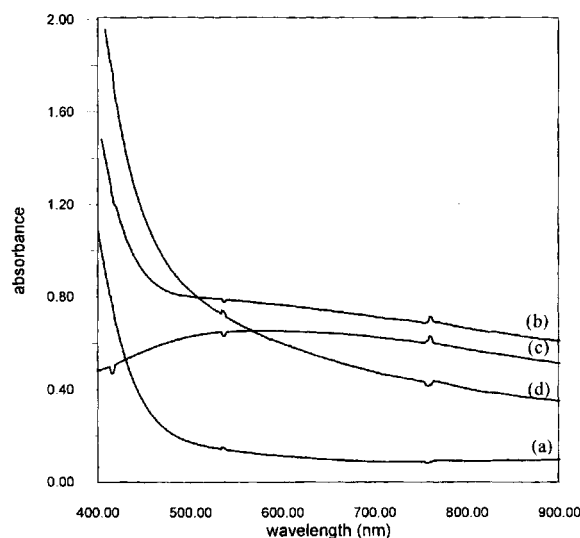
removal of lead ions was obtained after one hour of illumination (Table 1). When the surface was modified with MPA the conversion of trapped electrons into MV^{+} was not observed, indicating that the potential of trapped electrons was > -0.443 V.

Concurrently with lead reduction, the surface modifier is oxidized by photogenerated holes and this oxidation results in the formation of sulphydryl and disulphide anion radicals (RS· and RSSH). Serious difficulties were encountered in the determination of the oxidation potentials of surface modifiers by standard electrochemical techniques.[16] However, their oxidation potentials were determined by measuring the equilibrium constants of. the first electron transfer processes and were found to rise in the series: cysteine $(0.92)^{17}$ < mercaptoacetic $(1.347\,V)^{18} \approx$ mercaptopropionic $(1.359\,V)^{16} \approx$ thiolactic acid. Thus, cysteine is the surface modifier that is most easily oxidized, while all other surface modifiers that were examined have similar oxidation properties. Cyclic voltametry of these compounds with glassy carbon electrodes as working electrodes are shown in Fig. 6. As these systems are close to being irreversible systems, the thermodynamic data such as standard potentials are not available, and the system can furnish only kinetic information. However, the onset of the current for all three compounds coincides with the oxidation potential of a one electron oxidation step thermodynamically determined by Armstrong, *et al.*[15,16] From these potential data it can be expected that adsorption of cysteine leads to the most effective accumulation of electrons and the most rapid reduction of heavy metal ions present in the solution. However, we have found that the potential of

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Table 1. Precipitation of metallic lead on TiO_2 modified with different surface derivatives. See the Experimental section for details.

| Surface modifier	Standard potential (V)	$E°(Pb^{2+}$/surf. modifier) (V)	Atmosphere	Illumination time and wavelength	Pb^{2+}: remaining concentration (M)	Precipitate color	Comment
None			N_2	No	2.46×10^{-4}	White	Adsorption
None			N_2	1 h, UV	2.57×10^{-4}	White	Adsorption
Cysteine	0.92	-0.252	N_2	1 h, UV	1.02×10^{-4}	Brown	Reduction
Cysteine	0.92	-0.252	O_2-N_2	1 h, UV	1.60×10^{-4}	Beige	Slow reduction
MAA	1.347	-0.275	N_2	1 h, UV	1.52×10^{-4}	Beige	Slow reduction
MPA	1.359	-0.455	N_2	1 h, UV	2.13×10^{-5}	White	Strong adsorption
TLA	~1.3	-0.470	N_2	1 h, UV	2.15×10^{-5}	Brown	Reduction
TLA	~1.3	-0.470	N_2	No	3.35×10^{-5}	White	Strong adsorption
TLA	~1.3	-0.470	O_2-N_2	1 h, UV	3.2×10^{-5}	Brown	Reduction
TLA	~1.3	-0.470	N_2	2 h, VIS	2.9×10^{-5}	Brown	Reduction
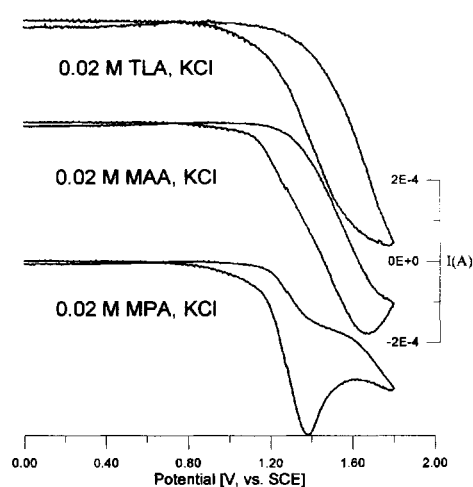
Fig. 6. Cyclic voltammetry waves of 0.1 M surface modifiers: (top) thiolactic acid; (middle) mercaptoacetic acid; (bottom) mercaptopropionic acid. Scanning speed was 100 mV s⁻¹.

a surface modifier is not a determining step for metal reduction on TiO_2. Furthermore, we think that the crucial parameters are the trade off between enhanced redox properties of TiO_2 and metal ions by surface modification. If we compare the results in Table 1 for MPA and TLA, we can see that they both have similar oxidation potentials, adsorption properties, and similar effects on the shift of the potential of lead ions. However, as we mentioned previously, they have different effects on the potential of TiO_2. TLA shifts the reduction potential of TiO_2 to < -0.45 V which is enough to reduce the Pb^{2+}-TLA complex. MPA, on the other hand, does not shift the potential of TiO_2 enough to reduce the Pb^{2+}-MPA complex of -0.45 V. Passive sorption of metal ions influences significantly the kinetics of the metal reduction. From Table 1 it can be seen that in the case of strong adsorption, the reduction of metal ions can be obtained in the presence of oxygen, although the reduction of oxygen is a more thermodynamically favorable process. These results can be explained by steric hindrance of the surface modifier for oxygen adsorption and therefore kinetic inhibition of direct reaction of

trapped electrons and molecular oxygen. It should be noted also that excitation of a charge transfer complex between TLA and TiO_2 with visible light leads to the reduction of metallic lead (Table 1).

Deposition of Cadmium. Redox potentials of TiO_2 are affected after surface modification with TLA to the extent that precipitation of metallic cadmium was observed after illumination of aqueous solutions containing cadmium ions $[E°(Cd^{2+}/Cd) = -0.401$ V$]$. Precipitation of metallic cadmium was even more surprising because complexation of metallic ions with mercapto-carboxylic acids leads to a negative shift of the redox potential (Fig. 7). After 30 min of illumination with UV light, the spectrum of the solution changed to a spectrum characteristic of metallic cadmium, distinct from the spectrum of trapped electrons (Fig. 8). We checked for formation of metallic cadmium by the method proposed by Henglein.[19] This method is based on the fact that cadmium deposited on the small particle colloid is very reactive and can reduce methylviologen completely [eqn. (2)]. As the reduction potential of $MV^{+·}$ is quite

$$2MV^{2+} + Cd^0 \rightarrow 2MV^{+·} + Cd^{2+} \qquad (2)$$

negative, any other stable compound like the oxide or sulphide of cadmium cannot reduce methylviologen. We have measured the concentration of $MV^{+·}$ produced from the metallic cadmium to be 4×10^{-4} M. However, under the same conditions X-ray spectroscopy (EXAFS and XANES) failed to detect any change after illumination.[20] As XANES and EXAFS are very important tools for the determination of the oxidation states of other metals with lower reduction potentials that cannot undergo the reaction with methylviologen, we are currently trying to understand this discrepancy. We suspect that we have not yet optimized the conditions to improve the ratio between reduced vs. non-reduced metal in the X-ray spectroscopy experiments.

Conclusions

Analysis of the structural, dynamic and redox properties of surface modified TiO_2 colloidal particles have indi-
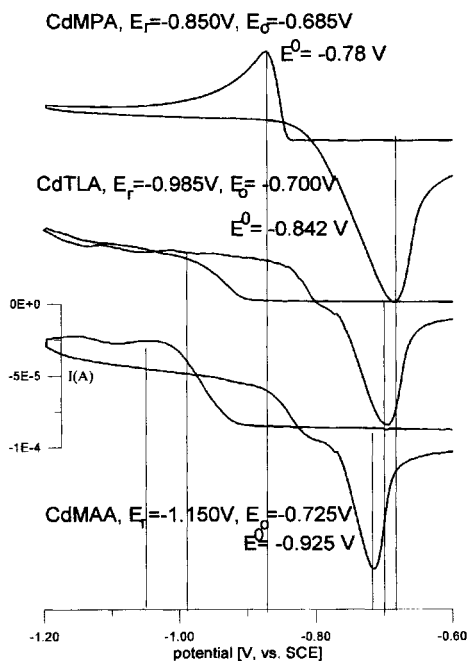
CdMPA, E$_r$=-0.850V, E$_o$=-0.685V

E^0= -0.78 V

CdTLA, E$_r$=-0.985V, E$_o$= -0.700V

E^0= -0.842 V

0E+0

-5E-5   I(A)

-1E-4

CdMAA, E$_r$=-1.150V, E$_o$=-0.725V

E^0= -0.925 V

-1.20   -1.00   -0.80   -0.60
potential [V, vs. SCE]

Fig. 7. Cyclic voltammetry waves of cadmium ion complexes with 1:1 different surface modifiers: (top) mercaptopropionic acid; (middle) thiolactic acid; and (bottom) mercaptoacetic acid. E_r represents the cathodic deposition potential for metallic cadmium, E_o represents anodic oxidation potential of metallic cadmium in the presence of surface modifiers and $E°$ represents the standard potential of the quasi-reversible couple.

Fig. 8. Deposition of metallic cadmium with illumination of thiolactate modified TiO$_2$. Absorption spectra of (a) 2×10^{-2} M thiolactate modified TiO$_2$ (0.2 M); (b) illuminated for 30 min with a 300 W Xe-lamp in the presence of 1×10^{-2} M Cd(ClO$_4$)$_2$. For comparison the absorption spectrum of electrons trapped on TiO$_2$ obtained upon illumination of TLA modified TiO$_2$ is shown as a dotted line; (c) after illumination 0.01 M methylviologen was added to (b) and the characteristic spectrum of the monovalent cation radical of methylviologen with its absorption maximum at 605 nm appeared.

cated principles for design of an optimal surface modifier for the reduction of heavy metal ions such as lead or cadmium. It was found that the surface modifier must contain a carboxy group to bind to the colloid surface and at the same time to bind Pb^{2+} and Cd^{2+} ions. The surface modifier has to have a hole trap that enhances the photogenerated charge pair separation distance. A mercapto group in the α position enhances the binding strength of a surface modifier and consequently enhances the adsorption of both surface modifier and heavy metals to small particle TiO$_2$ colloids. Formation of a charge transfer complex red-shifts the absorption threshold enhancing utilization of the solar spectrum. In these systems, side hydrocarbon groups, such as the –CH$_3$ group in TLA, provide a trapping site for holes that can be used for the design of a system in which the hydrophobic aliphatic or aromatic part of a surface modifier will be selectively used for the oxidation of organic compounds and a carboxy group for the reduction of heavy metal ions. It was found that surface derivatives modify the redox properties of TiO$_2$ particles if the surface modifier is an electron-donating species, and that the crucial parameter for effective reduction and hence removal of heavy metal ions is the trade off between enhanced redox properties of TiO$_2$ and metal ions by surface modification.
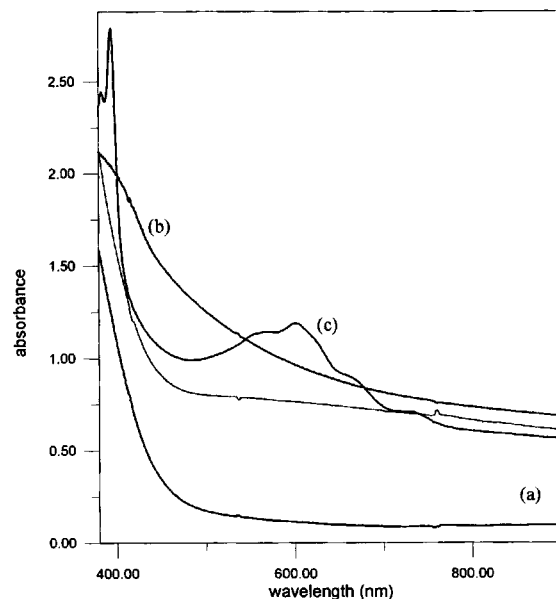
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