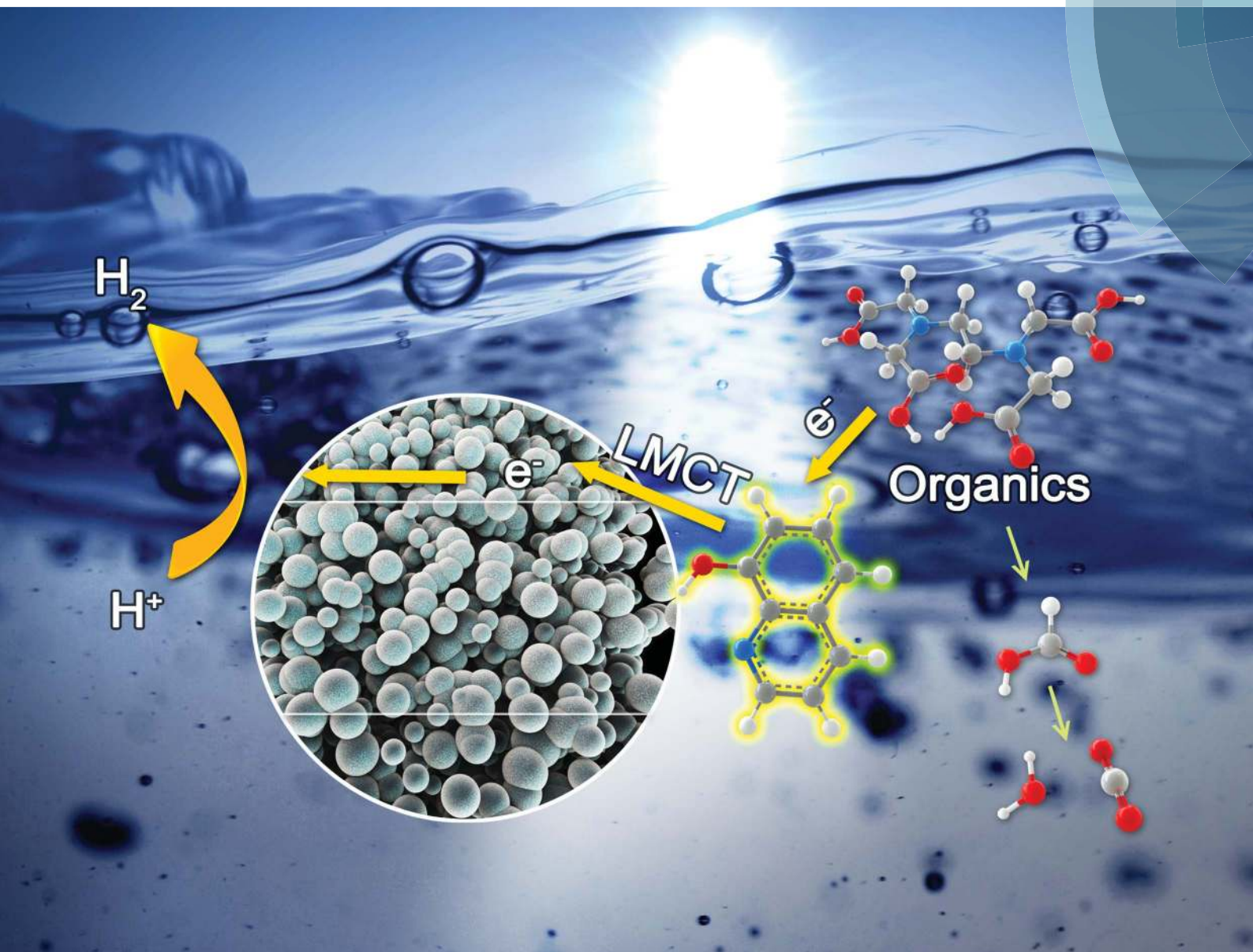


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MINIREVIEW

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Visible light driven photocatalysis mediated via ligand-to-metal charge transfer (LMCT): an alternative approach to solar activation of titania

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Visible light driven photocatalysis mediated *via* ligand-to-metal charge transfer (LMCT): an alternative approach to solar activation of titania

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Visible light harvesting or utilization through semiconductor photocatalysis is a key technology for solar chemical conversion processes. Although titania nanoparticles are popular as a base material of photocatalysis, the lack of visible light activity needs to be overcome. This mini-review is focused on an uncommon approach to visible light activation of titania: the ligand-to-metal charge transfer (LMCT) that takes place between TiO₂ nanoparticles and surface adsorbates under visible light irradiation. We discuss a basic concept of photoinduced LMCT and the recent advances in LMCT-mediated visible light photocatalysis which has been applied in environmental remediation and solar energy conversion. Although the LMCT processes have been less investigated and limited in photocatalytic applications compared with other popular visible light activation methods such as impurity doping and dye sensitization, they provide lots of possibilities and flexibility in that a wide variety of organic or inorganic compounds can form surface complexes with TiO₂ and introduce a new absorption band in the visible light region. The LMCT complexes may serve as a visible light sensitizer that initiates the photocatalytic conversion of various substrates or the self-degradation of the ligand complexes (usually pollutants) themselves. We summarized and discussed various LMCT photocatalytic systems and their characteristics. The LMCT-mediated activation of titania and other wide bandgap semiconductors has great potential to be developed as a more general method of solar energy utilization in photocatalytic systems. More systematic design and utilization of LMCT complexes on semiconductors are warranted to advance the solar-driven chemical conversion processes.

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Broader context

Semiconductor photocatalysis driven by solar light has great potential for energy and environmental applications. Wide band-gap semiconductor titania is a popular base material for photocatalysis, but does not absorb in the visible light region. Dye-sensitized TiO₂ has been frequently studied for solving this problem. However, successful dye sensitizers are mostly limited to the noble metal-based polypyridyl complexes (e.g., Ru(bpy)₃²⁺ derivatives), which restricts large-scale practical applications. Low-cost sensitizers such as metal-free organic dyes or organometallic complexes are being developed as alternatives. In contrast to the common dye sensitization, another type of sensitization based on the ligand-to-metal charge transfer (LMCT) between surface adsorbates and TiO₂ nanoparticles under visible light irradiation has been proposed but far less studied compared to the popular dye sensitization process. However, the uncommon LMCT sensitization has many advantages in that a wide variety of organic or inorganic compounds (that do not absorb visible light) can form surface complexes with TiO₂ and introduce new absorbance bands in the visible light region unlike the case of dye sensitization where the sensitizer itself should absorb the visible light. The LMCT-mediated activation of titania and other wide bandgap semiconductors has significant potential to be developed as a more general method of solar energy utilization in photocatalytic systems.

1. Introduction

TiO₂ photocatalysis has been extensively studied because of its successful performance in environmental remediation and solar chemical conversion and demonstrated to be a technically viable process to utilize solar energy.^{1–3} In terms of

environmental remediation, it can be applied to oxidative degradation of organic pollutants,^{4–6} reduction of heavy metal ions,^{7–9} indoor air purification,^{10–12} bacterial inactivation,^{13–15} *etc.* On the other hand, water splitting and CO₂ reduction driven by semiconductor photocatalysis (or artificial photosynthesis) have emerged as a hot issue to solve the problems of energy crisis and global warming.^{16,17} TiO₂ has excellent properties suitable for a practical material such as non-toxicity, easy availability and low cost, photo(electro)chemical stability, and band positions that can drive a wide range of photoinduced redox reactions. However, the main drawback of TiO₂ is the

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relatively large band-gap (~ 3.2 eV for anatase and ~ 3.0 eV for rutile), which only allows the absorption of UV light ($< 5\%$ of solar energy). Tuning the optical response of titania to the visible light region ($\sim 45\%$ solar energy) is indispensable. For the modification of wide bandgap semiconductors, doping (or co-doping) of metal or nonmetal elements^{18–20} and preparation of solid solutions^{21–23} are the common strategies. The foreign dopants introduced into the lattice may create some intermediate energy levels within the forbidden bandgap, which induces visible light absorption *via* the electronic transition between the band and the impurity levels. TiO₂ can also be sensitized by coupling with dyes^{24–26} or other narrow bandgap semiconductors like CdS, WO₃ and CuO.^{27–29}

Another method of visible light activation of wide bandgap semiconductors is the sensitization by surface adsorbates (or complexes) that do not absorb visible light by themselves, which has been much less investigated than the above methods. In this process, the visible light-induced charge transfer occurs from the HOMO of adsorbates to the conduction band (CB) of TiO₂, which is referred to as the ligand-to-metal charge transfer (LMCT) process.³⁰ Scheme 1 compares the typical dye sensitization with the LMCT process under visible light irradiation. The photochemical process of dye sensitization is initiated by the HOMO–LUMO photoexcitation of dye molecules which are

preadsorbed onto the TiO₂ surface, followed by electron transfer from the excited dye to TiO₂ CB; the oxidized dye is subsequently regenerated when there are suitable electron donors (Scheme 1a). Various dyes that have been tested for the sensitized TiO₂ include ruthenium bipyridyl derivatives,^{31–33} metal porphyrins,^{34–36} and metal-free organic dyes.^{37–39}

In the case of LMCT sensitization, the electron is photoexcited directly from the ground state adsorbate (without involving the excited state of the adsorbate) to TiO₂ CB. The oxidized adsorbate (with the hole left) could be further degraded into smaller molecules. Otherwise, it would be regenerated by the recombination with the photoexcited electron (back electron transfer) or by reacting with suitable electron donors available in the medium (Scheme 1b). The formation of such LMCT complexes on TiO₂ is usually accompanied by the appearance of a visible light absorption band, which is not seen with either the adsorbate or TiO₂ alone. Because electrons are transferred from the HOMO of the adsorbate to TiO₂ CB in the LMCT sensitization, the HOMO level of the adsorbate (relative to the CB edge) is an important factor in determining the visible light absorption whereas the HOMO–LUMO gap determines the visible light absorption in the dye sensitization. Therefore, unlike the case of dye sensitization where the sensitizer itself should absorb the visible light,



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conductor photocatalysis and photoelectrochemistry for solar energy conversion.

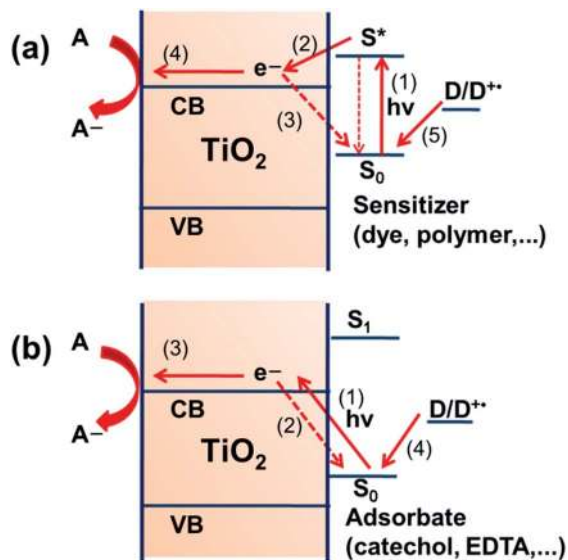


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1996–98), he joined the faculty of the School of Environmental Science and Engineering, POSTECH as an assistant professor (1998), and then was promoted to associate professor (2003) and full professor (2008). He has published more than 190 papers in peer-reviewed journals, which have been cited over 16 000 times (with H-index of 52) to date. He was awarded the Young Scientist Award from the Korean Academy of Science and Technology (2006), the Lectureship Award for Asian and Oceanian Photochemists from the Japanese Photochemistry Association (2008), and the Namgo (Jong-Ryul Lee) chair professorship from POSTECH (2012). He was elected as Fellow of the Korean Academy of Science and Technology in 2013. Currently, he is serving as an Editor of Journal of Hazardous Materials (Elsevier, since 2008). He has also served the editorial advisory board of Energy and Environmental Science (Royal Society of Chemistry, since 2008) and Journal of Physical Chemistry (American Chemical Society: 2009–2011).



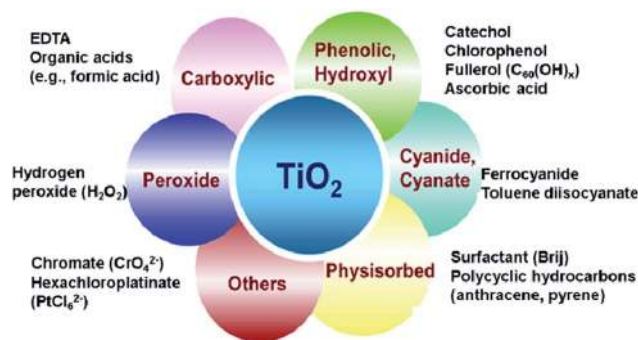
Scheme 1 The schematic illustration of two similar types of visible light sensitization of TiO_2 . (a) Dye sensitization: (1) excitation of the dye by visible light absorption, (2) electron transfer from the excited state of the dye to TiO_2 CB, (3) recombination, (4) electron transfer to the acceptor, and (5) regeneration of the sensitizer by an electron donor. (b) LMCT sensitization: (1) visible light-induced LMCT transfer, (2) recombination, (3) electron transfer to the acceptor, and (4) regeneration of adsorbates by an electron donor. S, D, and A represent the sensitizer (or adsorbate), electron donor, and electron acceptor, respectively. (S_0 : ground state, S^* and S_1 : excited state of the sensitizer/adsorbate).

a variety of organic or inorganic compounds (that do not absorb visible light) with suitable HOMO levels can be potential LMCT sensitizers. This gives the LMCT sensitization a great deal of flexibility in its design and application. In addition, this process may be particularly useful for the environmental remediation, since a variety of synthetic organic pollutants (with functional groups) can form LMCT complexes with the surface of metal oxide minerals. Solar irradiation on them can induce the degradation of the organic pollutants (ligands themselves) through the interfacial LMCT.

While many insightful review articles and books on TiO_2 -based photocatalysis have been published,^{1-3,40-49} no report is specifically focused on the utilization of the LMCT process in TiO_2 -based photocatalysis. This mini-review attempts to introduce and discuss recent findings and advances in LMCT complexes on TiO_2 as a means of visible light activation of photocatalysts. The LMCT complexes on TiO_2 have been tested with various surface modifiers (see Scheme 2). Some recent studies on the CT-complex modified TiO_2 are summarized according to the kind of linkage functionalities in Table 1.

2. Surface complexes on TiO_2 that induce visible light absorption

A number of studies on surface complexation of TiO_2 have been carried out to investigate the LMCT-induced visible light absorption. Most of the surface complexation induces visible



Scheme 2 Various kinds of functionalities forming LMCT complexes on the TiO_2 surface.

light absorption tailing to around 600–650 nm. The optical absorption intensity for one complex is also influenced by the properties of TiO_2 (e.g., size, surface structure). Rajh's group observed that the overall absorption in dopamine-complexed colloids with different particle sizes was enhanced by decreasing the particle size from 15 nm to 4.5 nm. The intensity of absorption was found to be proportional to the fraction of the surface Ti atoms and correlated with the number of surface sites in nanocrystalline TiO_2 .^{50,51} The characteristics of LMCT complexes (e.g., binding mode, electronic structure, optical response, charge transfer efficiency and photochemical stability) are closely related to the structure of ligands. The possible binding modes of representative complexes such as phenol, catechol, alcohol and carboxylate on the TiO_2 surface are shown in Scheme 3. These relatively electron-rich adsorbates having functional groups such as hydroxyl or carboxyl groups induce the appearance of LMCT bands in the visible light region upon surface adsorption. The most common characteristic of LMCT complex formation is the strong electronic coupling between the molecular orbitals of the adsorbate and the energy band of the supporting solid surface.⁵² The presence of the chemical linkage between the adsorbate and the surface strengthens the electronic coupling. When the adsorbates are less electron-rich, the LMCT band tends to appear in the UV region.⁵³

2.1 Phenolic and hydroxyl linkage

Phenolic compounds can easily form complexes with TiO_2 nanoparticles *via* their hydroxyl groups. The binding through the hydroxyl group enables strong coupling because only a single oxygen atom separates the phenolic ligand from the TiO_2 surface. The complex formation between TiO_2 and phenol extends the absorption into the visible light region as apparently indicated by the color change. A typical example is the TiO_2 -catechol complex, which has been well studied theoretically and experimentally.⁵⁴⁻⁵⁹ Catechol forms a complex with TiO_2 through several possible binding modes (as shown in Scheme 3) and introduces absorbance around 420 nm with a tail extending to 600 nm, which is ascribed to the LMCT transition. The bidentate binding is more stable than the monodentate mode and the former provides a stronger light

Table 1 Some recent studies on the LMCT complexes on TiO₂

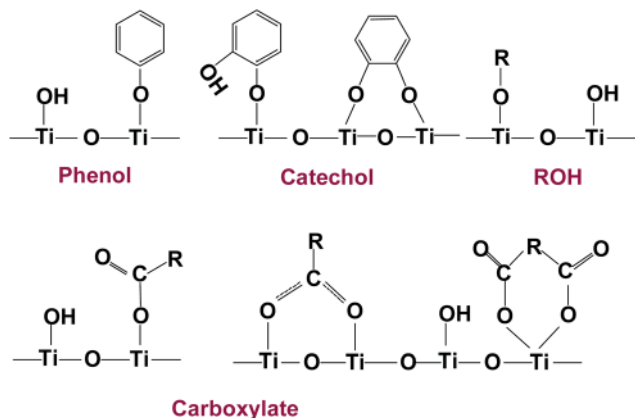
Functional group	Ligand	Key findings/applications	Ref.	
Phenolic	Catechol	Ultrafast electron-transfer dynamics analysis indicates that back electron transfer at the CT complex in catechol-TiO ₂ nanoparticles is slower compared to that at the intramolecular CT complex ([Ti(cat) ₃] ²⁻) because of the delocalization of electrons into other Ti centers in TiO ₂ nanoparticles.	54	
		<i>In situ</i> photoelectrochemical and spectroscopic techniques reveal two configuration modes of the CT complex (chelated and molecularly adsorbed), whereas only the chelate species from the CT complex were responsible for sensitization to the visible.	55	
		Direct observation of the interfacial CT complex in aqueous suspension by second-harmonic spectroscopy reveals a CT band centered at 2.72 eV (456 nm).	56	
		Zeolite-encapsulated TiO ₂ clusters by complexation with organic molecular modifiers containing OH groups that can strongly bind with titanol groups (>TiOH) exhibit enhanced photocatalytic activity.	57	
		Femtosecond fluorescence anisotropy measurements observe the localized CT excitation for catechol-sensitized TiO ₂ nanoparticles.	58	
		Resorcinol, quinol	Femtosecond transient absorption measurements demonstrate the bridging geometry influence on the CT efficiency in enediol-TiO ₂ systems (catechol, resorcinol and quinol), in which the CT transition strength is reduced in the system of resorcinol-TiO ₂ and quinol-TiO ₂ because of the reduced overlap between the HOMO localized on the enediol and the conduction band of TiO ₂ .	59
		Pyrogallol, gallic acid	FTIR spectroscopy investigates the binding structures of catecholate type ligands on TiO ₂ particles and finds the optimal geometry for chelating surface Ti atoms through bidentate bridging complexes.	67
		Salicylic acid	Femtosecond fluorescence anisotropy measurements observe the delocalized nature of CT excitation for salicylic acid-sensitized TiO ₂ nanoparticles.	58
		Phenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol	The existence of surface CT-complex formation between TiO ₂ and phenols and the CT mediated self-degradation of phenols under visible light are demonstrated.	68–70
		Dopamine	Femtosecond fluorescence measurements observe localized CT excitations for dopamine-sensitized TiO ₂ nanoparticles.	58
			Upon removal of coordinately unsaturated Ti sites at the TiO ₂ nanoparticle surface, the excess injected electrons are either weakly localized on the shallow lattice sites or delocalized in the conduction band of TiO ₂ nanoparticles.	51
			The major reactive oxygen species (ROS) produced upon illumination of TiO ₂ -dopamine is superoxide anions formed from the reaction of photogenerated electrons with molecular oxygen.	71
		Alizarin, methyl-catechol, <i>tert</i> -butyl-catechol	All enediol ligands form CT complexes and the change of optical absorption spectra is proportional to the density of delocalized π electrons and the dipole moment of surface-bound titanium-enediol ligand complexes.	50
		Fullerol	Fullerol can activate TiO ₂ under visible-light irradiation through the “surface-complex CT” mechanism, and the photocatalytic application for the reduction of Cr(vi), degradation of 4-chlorophenol, and H ₂ production is demonstrated.	72
		Sulfocalixarene	Sulfocalixarene plays a role in linking dyes and TiO ₂ due to the formation of surface complexes with TiO ₂ and providing the ion exchange capacity for adsorption of dyes.	73
Calixarene	The photoluminescence study demonstrates the strong stability of calixarene-Ti complexes due to the multiple covalent connections and suggests a surface-dipole governed electronic quenching phenomenon.	74		
1,1'-Binaphthalene-2,2'-diol	Binaphthol-modified TiO ₂ shows photochemical hydrogen evolution from aqueous triethanolamine solutions under visible-light irradiation.	75		
C ₁₁ -Resorcinarene	The adsorption of C ₁₁ -resorcinarene onto the surface of TiO ₂ particles induces the optical absorption in the visible range corresponding to LMCT transition within the TiO ₂ -C ₁₁ -resorcinarene complex.	76		
8-Hydroxyquinoline	8-Hydroxy-orthoquinoline modified anatase TiO ₂ generates H ₂ in a sacrificial water reduction system using visible light.	30		
Hydroxyl	Cyclodextrin (β -CD)	The TiO ₂ - β -CD complex exhibits enhanced and selective photocatalytic degradation of RhB and bisphenol under visible light.	77	
		The catalytic degradation of paracetamol can be significantly enhanced (~2.3 times) under visible light irradiation in TiO ₂ - β -CD suspension.	78	
	Ascorbic acid	EPR measurements demonstrate that the donating site in the CT complex is the ascorbate modifier, while the accepting site is the conduction band of TiO ₂ .	66	

Table 1 (Contd.)

Functional group	Ligand	Key findings/applications	Ref.
Poly-hydroxyls	Benzylic alcohols	Upon illumination of the ascorbic acid-complexed TiO ₂ electrode, ascorbic acid injects electrons into the conduction band of the semiconductor, giving rise to electrical current.	79
	Novolac phenolic resin	The highly efficient and selective photocatalytic oxidation of benzyl alcohol and its derivatives (substituted with -OCH ₃ , -CH ₃ , -C(CH ₃) ₃ , -Cl, -CF ₃ and -NO ₂) into corresponding aldehydes are realized on TiO ₂ in the presence of O ₂ under visible light irradiation.	80
	Resol phenolic resin	Thin layer coating of phenolic resin on TiO ₂ particles induces visible light photocatalytic activities (e.g., H ₂ production, 4-CP degradation and photocurrent generation).	82
		Deposition of TiO ₂ particles onto a mesoporous resin matrix forms complexation at the interface, which shows visible light photocatalytic activity for the degradation of dyes.	83
Carboxylic	Ciprofloxacin and related analogues	Ciprofloxacin and related analogues (harmful antibacterial agent) can be degraded under visible light <i>via</i> the surface complex formation on TiO ₂ .	85
	Ethylenediaminetetra-acetic acid (EDTA), sodium acetate, triethanolamine	The CT complex between TiO ₂ and EDTA (or formic acid) reduces Cr(vi) or protons under visible light.	84
	S-1-Dodecyl-S'-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate (DDAT)	DDAT-modified TiO ₂ enhances the efficiency for the photocatalytic degradation of 2,4-dichlorophenol compared with the pure TiO ₂ under visible-light.	89
Peroxide	Organic acids (oxalic acid, formic acid, lactic acid, malic acid, citric acid, tartaric acid)	Visible light-induced reduction of Cr(vi) over TiO ₂ is achieved through surface modification with small molecular weight organic acids.	86
	H ₂ O ₂	Surface complexation of H ₂ O ₂ -TiO ₂ induces the generation of \cdot OH radicals which can be used to degrade organic compounds (salicylic acid) under visible light.	90
		Ti- η^2 -peroxide on rutile TiO ₂ can convert 1-decene to 1,2-epoxydecane under visible light.	91
		The TiO ₂ -H ₂ O ₂ -visible light system can be applied to the degradation of persistent organic contaminants (linuron).	92
		The peroxide complex on TiO ₂ can be applied for the photooxidation of organic compounds (cyclohexane, nonyl aldehyde) under visible light.	93
		Amorphous TiO ₂ sol sensitized with H ₂ O ₂ exhibits photocatalytic activity for the degradation of methylene blue under visible light.	94
Cyanide	Iron cyanide	Electrons injected from Fe ^{II} (CN) ₆ ⁴⁻ to TiO ₂ nanoparticles under visible light are localized near the adsorbate.	100
	Fe(II), Re(III), Ru(II), Os(II), Mo(IV), W(IV) cyanide	Inorganic transition metal cyanide complexes anchored on the TiO ₂ surface extend their photoresponses to the visible region and can generate quite stable photocurrents under visible light.	101
Isocyanate	Toluene 2,5-diisocyanate (TDI), <i>m</i> -xylylene diisocyanate (<i>m</i> -XDI)	TDI modified TiO ₂ exhibits stronger visible light absorption and higher photocatalytic activity (for the degradation of methylene blue) than <i>m</i> -XDI modified TiO ₂ or pure TiO ₂ under visible light.	102
	Toluene 2,4-diisocyanate (TDI)	The TiO ₂ -TDI complex exhibits photostability and photocatalytic activity for the degradation of organics (phenol, 2,4-dichlorophenol, fluorescein and methyl orange)	103
Physisorbed	Arenes (phenanthrene, chrysene, anthracene)	Polycyclic hydrocarbon arenes (ArHs) can make CT-complexes with a dry TiO ₂ surface by physical adsorption.	114
	Polymeric benzene	Benzene can be activated by visible light ($\lambda > 455$ nm) in the presence of TiO ₂ , with the formation of carbonaceous polymeric deposits on the titania surface, which exhibit photoactivity for the degradation of 4-chlorophenol under visible light irradiation.	115
	Polyoxyethylene (Brij) surfactant	Complex formation between the surfactant functional groups and the TiO ₂ surface is responsible for the weak visible light absorption and the subsequent photoinduced electron transfer to CCl ₄ or Cr(vi).	116

absorption than the latter. The visible spectral band is resulted from the direct electronic transition from the HOMO (ground) state of catechol into the LUMO (the edge of CB) state of TiO₂ (Ti 3d orbital), bypassing the LUMO (excited) state of catechol. The binding mode of catechol-TiO₂ and its influence on the

molecular electronic structure were well investigated by a combined theoretical and experimental (scanning tunneling microscopy (STM) and UV photoemission spectroscopy (UPS)) method.^{60,61} The STM measurement showed that catechol molecules formed an ordered densely packed monolayer on the

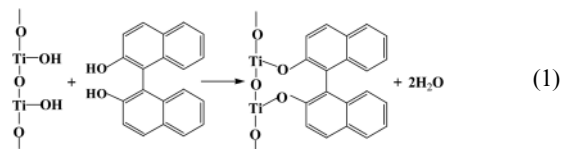


Scheme 3 The possible binding modes of representative complexes on the TiO_2 surface.

TiO_2 (110) surface and the UPS spectra of the adsorbed surface found that this overlayer gave rise to an additional electronic state (peak around 2.4 eV) above the TiO_2 VB edge, which was assigned to the HOMO of catechol. The other spectroscopic characterizations of the catechol complex have been carried out by transient absorption spectroscopy,^{54,62} fluorescence quenching,^{63–65} Raman spectroscopy⁵⁵ and electron paramagnetic resonance.⁶⁶ Other phenolic compounds that were reported to form the LMCT complexes include resorcinol and quinol,⁵⁹ pyrogallol and gallic acid,⁶⁷ salicylic acid,⁵⁸ 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol,^{68–70} dopamine,^{50,51,58,71} alizarin, methylcatechol and *t*-butylcatechol,⁵⁰ fullerol,⁷² sulfocalixarene,⁷³ calixarene,⁷⁴ 1,1-binaphthalene-2,2'-diol,⁷⁵ C_{11} -resorcinarene⁷⁶ and 8-hydroxyquinoline.³⁰ The substituting groups attached on the benzene ring (*e.g.*, $-\text{Cl}$, $-\text{NH}_2$, $-\text{OH}$, $-\text{COOH}$, $-\text{CH}_3$, and $-\text{C}(\text{CH}_3)_3$) vary in their electron donating (or withdrawing) properties and sensitively influence the optical absorption and charge transfer efficiency. For example, attaching electron donating groups (methyl or *tert*-butyl) onto catechol shifts the optical absorption of the TiO_2 -catechol complex towards longer wavelengths.⁵⁰ The substituent effect is related to the change of the dipole moment of surface-bound Ti-ligand complexes. Inducing the dipole moment on the surface shifts the electronic charge within the complex to render orbital overlap more intensely, and consequently shifting the absorption properties.⁵⁰

The CT complexes formed on TiO_2 through the phenolic linkage often induce visible light reactivity. For example, 4-chlorophenol that weakly adsorb on TiO_2 can be degraded under visible light, which can be ascribed to the LMCT (from adsorbed phenol to TiO_2 CB) induced oxidation of phenol.⁶⁸ Since phenolic compounds are a common class of organic pollutants, the fact that the phenolic compounds can be degraded under purely visible light irradiation (despite that neither phenol nor TiO_2 absorbs visible light) has an important implication for the photocatalytic degradation mechanism occurring on TiO_2 . However, it should be noted that the LMCT-induced degradation of phenolic compounds under visible light is much slower than that of bandgap-excited photocatalysis under UV irradiation.

On the other hand, the π -electron conjugation and bridging geometry of the phenolic ligands also strongly influence the charge transfer efficiency, surface binding properties, and complex stability. Notestein *et al.* reported that calix[4]arene (cyclic tetramers of phenol) grafted onto TiO_2 nanoparticles formed stable surface complexes with induction of visible light absorption (<560 nm).⁷⁴ The calixarenes are completely resistant to desorption in aprotic solvents or water and quite resistant to washing in alcohols due to the multiple covalent linkages. Ikeda *et al.* reported that 1,1'-binaphthalene-2,2'-diol ($\text{bn}(\text{OH})_2$) modified $\text{TiO}_2(\text{Pt})$ yielded H_2 from deaerated triethanolamine solution under visible light irradiation, whereas phenol- or catechol-complexed $\text{TiO}_2(\text{Pt})$ did not.⁷⁵ This can be ascribed to the enhanced electron transfer efficiency in the larger conjugating system of $\text{bn}(\text{OH})_2$ (eqn (1)).



Kaniyankandy *et al.* investigated the effects of the ligand bridging geometry on the interfacial electron transfer dynamics in the dihydroxyphenol- TiO_2 system (catechol, resorcinol and quinol with which the positioning of the two hydroxyl groups varies).⁵⁹ They found that CT efficiency decreased from catechol to resorcinol to quinol as indicated by the UV-visible absorption spectra (Fig. 1a), which was explained on the basis of a reduced overlap between the HOMO localized on the dihydroxyphenol and TiO_2 CB.

They also found that the rate of charge recombination (back electron transfer) decreases from catechol to quinol by measuring the transient absorption decay profiles at 620 nm (Fig. 1b). This was ascribed to the increased delocalization of the injected electrons as the distance between the bridge linkers

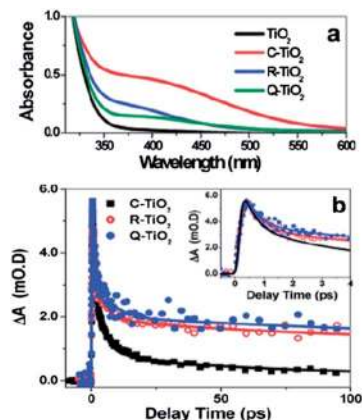
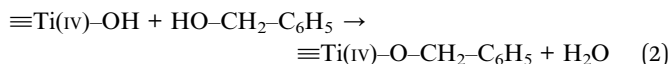


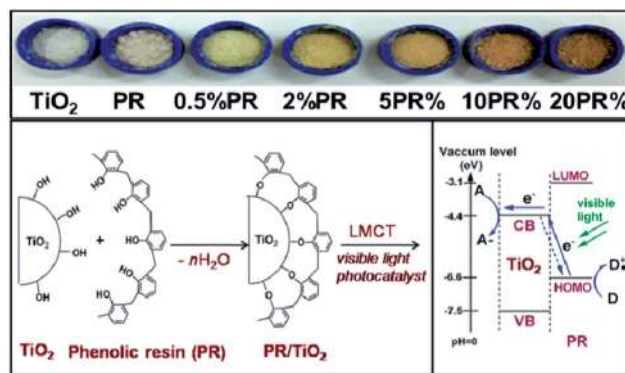
Fig. 1 (a): UV-visible absorption spectra of the catechol- TiO_2 (C- TiO_2), resorcinol- TiO_2 (R- TiO_2), and quinol- TiO_2 (Q- TiO_2) complexes. (b) Transient absorption time profiles (inset: shown at a shorter time scale) measured at 620 nm for the three dihydroxyphenol- TiO_2 systems in chloroform. Adapted with permission.⁵⁹ Copyright 2012 American Chemical Society.

increases. The fast recombination in the catechol case where delocalization is weak was attributed to the strong orbital coupling. This observation is important from the point of view of photocatalytic application as they proposed that control of electronic coupling by just varying the position of the bridge linkers can also enhance the electron transfer efficiency.

Organic compounds with hydroxyl groups such as cyclodextrin (β -CD),^{77,78} ascorbic acid,^{66,79} and benzylic alcohol and its derivatives⁸⁰ were also reported to form LMCT complexes with TiO_2 . They induce a weaker visible light absorption band compared to that of the TiO_2 -phenol complexes that have the π electronic system directly attached to the TiO_2 surface. The benzylic alcohols complexed on TiO_2 (eqn (2)) were selectively oxidized to aldehydes upon the injection of electrons to TiO_2 through the LMCT process under visible light.⁸⁰ β -CD can be grafted onto the TiO_2 surface through multiple hydroxyl linkages through physical adsorption or a photoinduced self-assembly method.^{77,78} In the latter method, the photoexcited TiO_2 surface has a tendency to associate strongly with available hydroxyls since polyhydroxyl compounds scavenge holes efficiently.⁸¹ After modification with β -CD, the hybrid material synthesized by the photoinduced self-assembly method exhibited a relatively higher absorption intensity in the visible region compared to that prepared by a physical adsorption method. The irradiation-assembled TiO_2 - β -CD increased the initial degradation rates of rhodamine B and bisphenol A under visible light ($\lambda \geq 420$ nm). A CT-complex was formed between β -CD and TiO_2 during the photoinduced self-assembly process. The complex subsequently generated superoxide radicals under visible light irradiation, which were the predominant reactive oxygen species.⁷⁷



LMCT complexes that are mostly anchored on the semiconductor surface through one or two functional groups often suffer from low stability. To enhance the stability of the complex, a polymer consisting of LMCT-forming monomer units can be employed since stronger LMCT complexes are formed through multiple anchoring bonds. For example, the LMCT complexation between phenols and TiO_2 can be maximized by employing a novolac type of phenolic resin (instead of monomeric phenols) (see Scheme 4).⁸² The multi-hydroxyl groups of the resin form a stronger binding and complexation with TiO_2 through condensation reaction and the CT occurs from the HOMO of the resin to TiO_2 CB as illustrated in Scheme 4. The phenolic resin is insoluble in water, which makes the TiO_2 -resin composite more stable in aqueous solution. The polymer-coated TiO_2 exhibits visible light photocatalytic activities for the degradation of organic pollutants and H_2 evolution from water. In a similar way, dispersing TiO_2 nanoparticles onto a mesoporous resin type of phenolic resin sphere can form a CT complex that absorbs visible light over a wide range (400–700 nm).⁸³ This TiO_2 -phenolic resin composite was fabricated by a solvothermal method, by which the TiO_2 particles were tightly grafted onto the surface of mesoporous



Scheme 4 Illustration of phenolic resin (PR) complexation onto a TiO_2 nanoparticle through condensation reaction and the proposed electron transfer pathways in the LMCT sensitization process. The color changes induced by PR complexation on TiO_2 with different PR loadings are also shown in the upper photo images. Adapted with permission.⁸² Copyright 2012 The Royal Society of Chemistry.

phenolic resin to form a uniform heterostructure. After TiO_2 loading under solvothermal conditions, the color of the hybrid sample became deep yellow. The hybrid nanocomposite also showed considerably high stability in the photocatalytic degradation of organic dyes.

2.2 Carboxylic linkage

The carboxylic acid group can be easily deprotonated to carboxylate anions ($-\text{COO}^-$) in aqueous solution, while the surface titanol group of TiO_2 is positively charged ($\equiv\text{Ti-OH}_2^+$) when the pH of the aqueous solution is lower than pH_{zpc} ($\text{pH}_{\text{zpc}} \sim 6$ for TiO_2).⁸⁴ Therefore, the electrostatic attraction of the carboxylate anions to the positive titanol group induces the complex formation. This complexation strongly depends on the pH of solution and is preferred at low pH.^{84–86} The TiO_2 -carboxylate complex has two possible configurations: monodentate vs. bidentate (Scheme 3). Formic acid is the simplest carboxylic acid that can make a CT complex on TiO_2 . Several studies have shown that formate anions in aqueous solution are bound to the TiO_2 surface mostly through a bidentate bridging coordination, and the monodentate complexation is less favored.^{87,88} The TiO_2 -EDTA complex favors the bidentate chelating coordination.⁸⁴ As for the complexation of acetic acid and oxalic acid with TiO_2 , bidentate mode is also known to be more stable than monodentate mode.^{52,88}

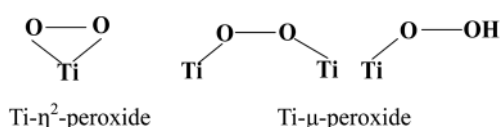
The carboxylic group is one of the most common functionalities (along with phenolic groups) found in various organic compounds and toxic pollutants. Therefore, the fact that it can form an LMCT complex on TiO_2 implies that the carboxylic compounds adsorbed on TiO_2 can have an intrinsic photocatalytic activity under visible light.^{84–86,89} For example, Paul *et al.* showed that the harmful antibacterial agents (ciprofloxacin and related analogues) could be degraded into smaller molecules under visible light *via* the surface complex formation on TiO_2 .⁸⁵ In this case, visible light absorption was extended to around 450 nm (for ciprofloxacin). However, the mineralization of the compound under visible light was not achieved because

the degradation byproducts were not further degraded under visible light. Wang *et al.* showed that several organic acids (tartaric acid, citric acid, malic acid, lactic acid, formic acid) could make surface complexes with TiO₂ (by inducing an absorption tail, extending to even 800 nm for the tartaric acid case) and utilized them for the reduction of toxic Cr(vi) to less harmful Cr(III).⁸⁶ Kim and Choi also demonstrated that the CT complexes formed between TiO₂ and common electron donors such as EDTA and formic acid (visible absorption edge: around 550 nm) could be applied to the reductive conversion of Cr(vi) to Cr(III) and protons to H₂ in water under visible light.⁸⁴

2.3 Hydrogen peroxide

Hydrogen peroxide can form a surface complex with TiO₂ through the condensation reaction (eqn (3)).⁹⁰ The TiO₂-H₂O₂ complex is formed in a wide range of pH (2–9.5), and H₂O₂ is adsorbed onto the TiO₂ surface more at pH 5.4 than at pH 2. Neutral pH is a more suitable condition than low pH for the condensation reaction. Many experiments on TiO₂-H₂O₂ complexation were also conducted at near neutral pH condition.^{91–94}

The TiO₂-H₂O₂ complex exists in two configurations: Ti-η²-peroxide and Ti-μ-peroxide (Scheme 5), which were confirmed by FT-IR experiments.^{91,95–97} The abundance of each configuration species depends on the TiO₂ phase. The TiO₂-H₂O₂ complex has a yellowish color and absorbs visible light up to 550 nm, but is not stable and highly reactive even under room light conditions.⁹¹ Through LMCT, an electron is transferred from the complexed H₂O₂ to TiO₂ CB under visible light and the injected electron subsequently reacts with another adsorbed H₂O₂ to generate a hydroxyl radical (Fig. 2a).⁹⁰ The generation of hydroxyl radicals was proven by EPR analysis (Fig. 2b), which implies that the system of TiO₂-H₂O₂-visible light can be applied to the degradation of persistent organic contaminants.



Scheme 5 The possible coordination structure of H₂O₂ adsorbed on the TiO₂ surface.

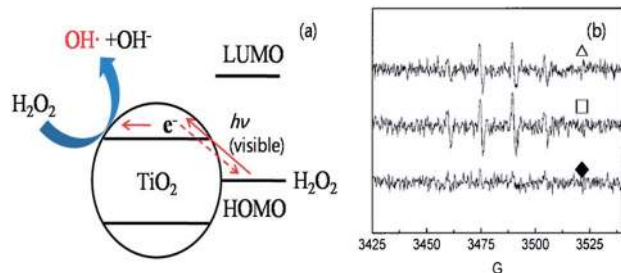
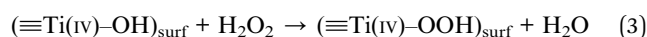


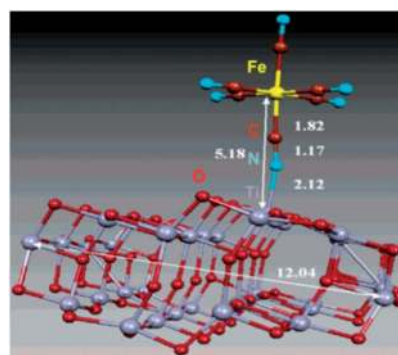
Fig. 2 (a) A possible hydroxyl radical generation mechanism via the TiO₂-H₂O₂ complexation under visible light. (b) EPR spectral change with increasing visible light irradiation ($\lambda > 420$ nm) time: (◆) dark, (□) 15 min, (△) 30 min. Adapted with permission.⁹⁰ Copyright 2001 American Chemical Society.

Rao *et al.* investigated the photocatalytic decomposition of Linuron, a phenyl-urea herbicide, and found that the degradation intermediates generated on TiO₂-H₂O₂ under visible light are similar to those produced in the TiO₂-UV system.⁹² The complete ring opening and 32% TOC removal were observed after 56 h irradiation in the TiO₂-H₂O₂-visible light system. The degradation of organics such as cyclohexane and methyl orange by the TiO₂-H₂O₂ complex was also studied by other groups although the mineralization of these compounds was not investigated in their study.^{93,94} The TiO₂-H₂O₂ LMCT system is a good example of how H₂O₂ can be activated to generate hydroxyl radicals by using visible light although neither H₂O₂ nor TiO₂ absorbs visible light. Although H₂O₂ may serve as an acceptor of CB electron (as shown in the upper left corner of Fig. 2a) in a typical TiO₂-UV system, it plays the role of electron donor on the contrary in the TiO₂-H₂O₂-visible light system with the production of OH radicals accompanied.



2.4 Cyanide/isocyanate and inorganic linkage

Metal cyanides like ferrocyanide, Fe^{II}(CN)₆⁴⁻, can bind to the TiO₂ surface through the ambidentate cyano ligand (Scheme 6). The complexation between the TiO₂ surface and ferrocyanide extends the photoresponse of TiO₂ to the visible region (to around 700 nm). Light sensitization of TiO₂ with metal cyanides is accomplished by metal-to-particle charge transfer (MPCT) and metal-to-ligand charge transfer (MLCT) pathways. MPCT is similar to LMCT in that light absorption promotes electrons from metal centers directly to TiO₂.^{98–100} The inorganic complex anchored on the TiO₂ surface is more stable than other organic complexes. For example, the TiO₂-Prussian Blue (ferric ferrocyanide) complex generates quite stable photocurrent for 3 days and its turnover number reaches more than 1000. Other transition metal cyanides such as Re^{III}(CN)₇⁴⁻, Ru^{II}(CN)₆⁴⁻, Os^{II}(CN)₆⁴⁻, Mo^{IV}(CN)₈⁴⁻, and W^{IV}(CN)₈⁴⁻ were also tested for the CT complexation with TiO₂ and exhibited photocurrent generation activity under visible light. They all generated stable photocurrent in the presence of electron donors and among



Scheme 6 Structure of a TiO₂-Fe^{II}(CN)₆⁴⁻ system in the monodentate configuration. White = main bond distance (Å), grey = Ti, red = O, turquoise = N, brown = C and yellow = Fe atoms. Adapted with permission.⁹⁸ Copyright 2004 American Chemical Society.

them, the sensitization of TiO_2 by $\text{Re}^{\text{III}}(\text{CN})_7^{4-}$, $\text{Ru}^{\text{II}}(\text{CN})_6^{4-}$, and $\text{Os}^{\text{II}}(\text{CN})_6^{4-}$ was the most effective. The maximum photocurrent efficiencies were obtained at pH 2 to 3 since the electrostatic attraction between the positively charged TiO_2 surface and the anion is an important factor for the complex formation.¹⁰¹

Surface complexation between TiO_2 and isocyanate groups ($-\text{N}=\text{C}=\text{O}$) has also been investigated. Jiang *et al.* examined the CT-complex between TiO_2 and toluene 2,4-diisocyanate (TDI) and showed that TDI is anchored on the TiO_2 surface *via* a bond of $-\text{NHCOOTi}-$ which is formed through the reaction of $-\text{NCO}$ and hydroxyl groups on TiO_2 (Fig. 3a).¹⁰² The CT-complex showed strong visible light absorption in 420–700 nm (Fig. 3b). The TiO_2 -TDI complex maintained a stable activity for the photocatalytic degradation of methylene blue for 40 h (Fig. 3c). Chen *et al.* also reported that the TiO_2 -TDI complex showed similar absorption characteristics and stability:¹⁰³ the photodegradation of 2,4-dichlorophenol was monitored as an activity test probe and the turnover number of the TiO_2 -TDI complex

reached 15.4 after 5 times of recycling under visible light irradiation. The TiO_2 -TDI complex was not degraded significantly after 240 min photoreaction according to the FTIR analysis. Although the detailed mechanism was not thoroughly investigated, the photodegradation of 2,4-dichlorophenol, phenol, fluorescein and methyl orange was achieved with the TiO_2 -TDI complex under visible light.

Kisch and coworkers investigated the photosensitization of titania by noble metal (Pt^{4+} , Rh^{3+} , Au^{3+}) chloride surface complexes under visible light.^{104–106} The hybrid photocatalysts are capable of degrading 4-chlorophenol under visible light with sufficient stability against decomplexation. It was proposed that the surface complex ($\equiv\text{TiOPt}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})$) firstly undergoes homolytic platinum–chloride bond cleavage *via* LMCT excitation yielding a Pt^{III} intermediate and chlorine atoms, then subsequent electron injection from Pt^{III} to the TiO_2 CB occurs and chlorine atoms abstract electrons from organic pollutants, resulting in the degradation of pollutants and the regeneration of the inorganic metal complex. Reduction of adsorbed dioxygen molecules by TiO_2 CB electrons through several steps leads to the production of reactive oxygen species as well.

The chromate(vi)- TiO_2 system has also been reported to have a visible light activity, which is ascribed to a unique LMCT phenomenon in chromate itself. This case is somewhat different from the cyanide and isocyanate complexes. The hexavalent chromium (chromate) is a highly toxic species and its photochemical reduction to Cr^{III} that is much less toxic has been frequently investigated.^{72,84,86,107–109} Visible light absorption of chromate, extending to *ca.* 500 nm, is attributed to LMCT excitation of chromate anions transferring electrons from O^{II} to Cr^{VI} . It has been proposed that chromate can serve as a visible light sensitizer of TiO_2 : the excited chromate injects a hole to TiO_2 VB, which is subsequently followed by the generation of OH radicals under visible light, which was confirmed by electron paramagnetic resonance investigation.¹¹⁰ The oxidation of 4-chlorophenol in aqueous phase and volatile organic pollutants like acetone and methanol in gas phase was demonstrated with a chromate-sensitized TiO_2 system under visible light.^{111–113}

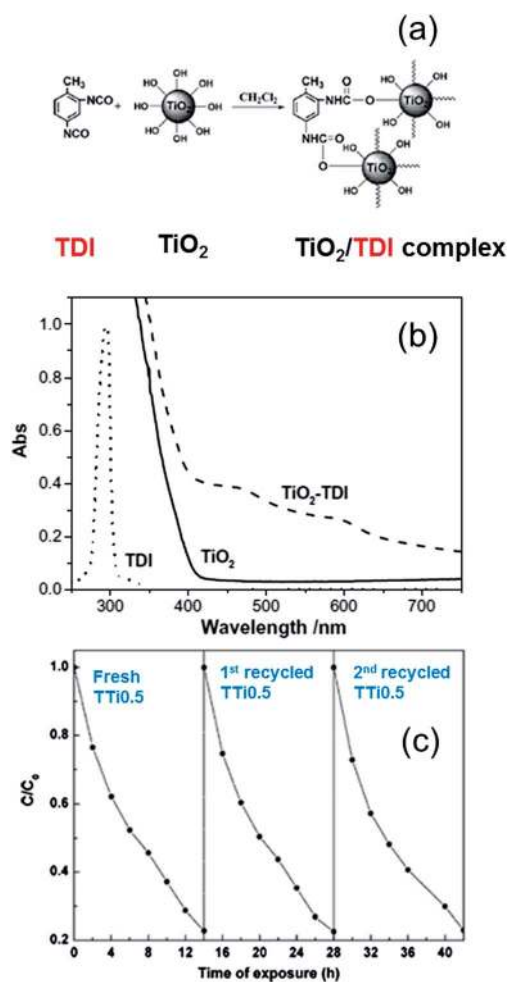


Fig. 3 (a) Schematic illustration of the formation process of the TiO_2 -TDI complex. (b) Diffuse reflectance UV-visible spectra of TiO_2 and TiO_2 -TDI complex and the absorption spectrum of TDI alone. (c) Photocatalytic degradation of methylene blue (50 ppm) with a recycled TiO_2 -TDI complex (where TTI 0.5 indicates that the molar ratio of TDI- TiO_2 is 0.5/1). Adapted with permission.^{102,103} Copyright 2009 Elsevier.

2.5 LMCT on TiO_2 in a physisorbed system

CT-complexation on TiO_2 can be even induced by physically adsorbed substrates, which is very different from most of CT-complex systems based on the chemisorption (through a bond formation) between the surface adsorbate and TiO_2 . Seo *et al.* reported that pure polycyclic arenes (chrysene, anthracene, pyrene and benzo[*a*]pyrene) can readily form 1 : 1 and 2 : 1 (arene dimer) CT-complexes with a dry TiO_2 surface.¹¹⁴ The new absorption band in the visible region (with pale brownish color) was assigned to a CT band between the arene compound and TiO_2 . The colored arene- TiO_2 complex could be reversibly bleached by desorbing the arenes without degrading the arene compounds, which indicates that the coloration is not resulted from the chemical change of the arene structure upon contact with TiO_2 . The arenes did not fluoresce on TiO_2 because of the electron transfer quenching whereas they did on BaSO_4 and

SiO₂. Another example of the visible light activity of the physisorbed CT-complex was reported with TiO₂ in benzene:¹¹⁵ visible light irradiation of a TiO₂ suspension in benzene for a prolonged time induced a color change (from white to brownish suspension), which was ascribed to the formation of polymeric benzene species on the titania surface. The CT-induced colorization process is described in Fig. 4. The CT induces the oxidation of benzene to benzene cation radicals (under visible light) and the subsequent polymerization of benzene radicals follows to form polymeric species on the TiO₂ surface. The *in situ* deposited polymeric benzene on TiO₂ under visible light exhibited not only a weak visible light absorption (Fig. 4c) but also a photocatalytic activity for the degradation of 4-chlorophenol under visible light. Two possible mechanisms are ascribed to explain the photocatalytic activity. One is the sub-bandgap transition from the surface states to the TiO₂ CB. The benzene molecules are thereby oxidized to benzene cation radicals, and photogenerated electrons reduce dioxygen to superoxide anion radicals. The other is the interaction between Ti–OH and/or Ti⁴⁺ and the π -electrons of the aromatic ring might lead to formation of a weak CT complex between the aromatic system and the Ti⁴⁺ metal center, which then facilitates oxidation under visible light irradiation.

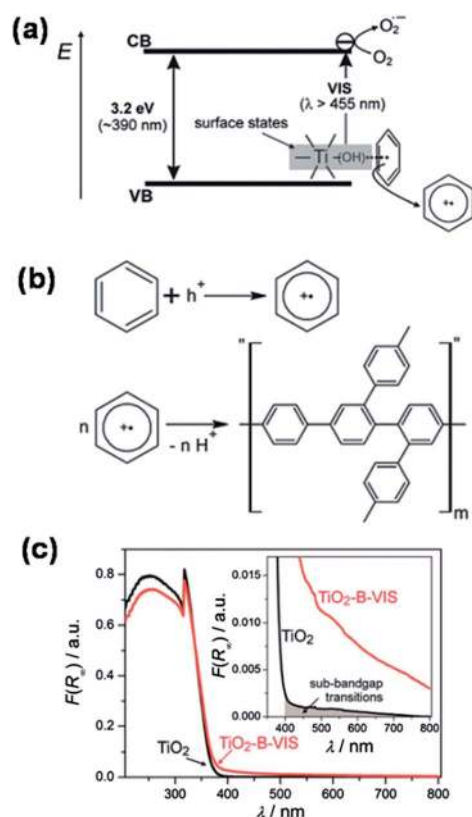


Fig. 4 (a) Illustration of visible light-induced oxidation of benzene in TiO₂ suspension; (b) suggested mechanism of formation of polymeric benzene deposits; (c) absorption spectra of TiO₂ and TiO₂-B-VIS (after irradiation in the benzene); the inset shows a magnification of the visible light region. Adapted with permission.¹¹⁵ Copyright 2012 The Royal Society of Chemistry.

The visible light-induced CT phenomenon was also observed in the physical mixture of TiO₂ nanoparticles and non-ionic surfactants with polyoxyethylene groups (Brij series) that do not absorb visible light at all by themselves.¹¹⁶ The surfactant-TiO₂ suspension exhibited a broad and weak absorption band in the visible region (320–500 nm) and, as a result, the visible light-induced electron transfer on surfactant-TiO₂ reductively degraded CCl₄ into Cl⁻ and CO₂ or reduced Cr(vi) to Cr(III). It was proposed that a complex formation between the surfactant functional groups [-(OCH₂CH₂)_n-OH] and the surface titanol groups is responsible for the weak visible light absorption and the subsequent photoinduced electron transfer. The complexation was strongly dependent on the kind of surfactants and only Brij-series exhibited a measurable absorption band in the visible region and significant visible light reactivity.

All the above examples demonstrate that the weak physical interactions between organic compounds and TiO₂ surface often lead to visible light-induced CT although neither of the components absorbs visible light. This implies that the LMCT phenomenon taking place on the semiconductor surface is quite ubiquitous in the surface interactions with various organic and inorganic substrates regardless of the linkage bond formation.

2.6 Applications of LMCT in visible light photocatalysis

Creation of a new visible absorption band by CT-complex formation enables us to develop various TiO₂-based photocatalytic systems for environmental remediation and energy conversion. It can be conducted through either an oxidative or a reductive process. The most obvious example is the self-degradation of CT-complexes that are pollutants by themselves. Many organic pollutants that do not absorb visible light can possibly make CT-complexes with TiO₂. After injecting an electron into TiO₂ through the LMCT process, the organic molecule would be oxidized to cationic radical species which should be further degraded into smaller fragments (usually less toxic) or even mineralized in some cases.⁸⁵ In the presence of oxygen, the injected electrons can also reduce dioxygen molecules to generate strongly oxidizing species such as superoxide or hydroxyl radicals, which subsequently oxidizes organic pollutants in water.^{89,102,103} This should serve as the basis of visible light-induced photocatalytic oxidation on pure TiO₂. On the other hand, the electrons injected into TiO₂ can be utilized for the reductive conversion such as H₂ evolution from water. A toxic inorganic species like Cr(vi) can also be reduced by the CB electrons in TiO₂.^{72,84,86,107–109} The oxidative self-degradation and reductive transformation may simultaneously proceed in some cases, which might be a promising method for the development of LMCT-mediated environmental remediation.

2.7 Applications of LMCT in sensitized solar cells

The LMCT process can be applied to sensitized solar cells as well as photocatalysis: the direct injection of electrons from adsorbed ligands to semiconductor particles upon visible light irradiation and the collection of injected electrons on a working electrode as photocurrent in the solar cell assembly. Although

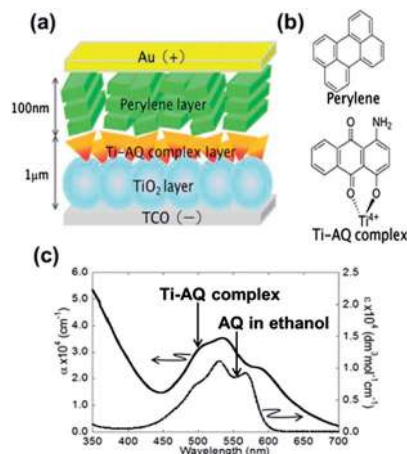


Fig. 5 Illustration of the TiO₂-anthraquinone (AQ)-perylene photo-voltaic cell (a); molecular structure of components (b); visible absorption spectra of AQ on TiO₂ and in ethanol solution. Adapted with permission.¹¹⁸ Copyright 2012 The Royal Society of Chemistry.

this review is mainly on photocatalysis, the solar cell application is briefly mentioned here because of its close similarity. LMCT-sensitized solar cells have not been much studied unlike the popular dye-sensitized solar cells because the solar energy-to-electricity conversion efficiency is only *ca.* 1.0% for LMCT sensitization, ten-fold lower than the common Ru-complex sensitized solar cells.¹¹⁷ The key limiting factor is that the back electron transfer from TiO₂ to the oxidized sensitizer is much faster than that in dye-sensitized solar cells. It was demonstrated that a large portion (>75%) of charge recombination occurs within a few picoseconds in the LMCT sensitization.⁵⁴

Tae *et al.* reported a strategy to increase the efficiency of the LMCT solar cells by attaching electron-donating groups such as (pyridine-4-yl)vinyl and (quinolin-4-yl)vinyl to catechol or its derivatives for obtaining the short-circuit current enhancement by 2–3 fold.¹¹⁷ Recently, a thin solid-state cell of organic-inorganic heterojunctions has been fabricated by forming a LMCT complex as the sensitizer monolayer at the interface of semiconductors.¹¹⁸ The hybrid thin-film solar cell generated a photovoltage of 1.2 V, yielding an energy conversion efficiency of up to 1.5%. They found that a CT-complex of Ti and anthraquinone (AQ) formed at the surface of TiO₂ works as an excellent visible-light sensitizer of photoelectric conversion in conjunction with an organic hole conductor (perylene) as shown in Fig. 5. AQ in ethanol solution has an absorption peak (at around 550 nm), originated from $\pi-\pi^*$ transition, while AQ on TiO₂ exhibits a bathochromic shift to longer wavelengths indicating that the electronic state of AQ is changed by its coordination to Ti⁴⁺ on the TiO₂ layer (Fig. 5c). The development of LMCT complexes for sensitized solar cells has much room for further enhancement and diversity.

3. Conclusions and outlook

Formation of CT-complexes between the TiO₂ surface and adsorbates can be utilized as a useful sensitization technology

for harvesting solar visible light because a wide variety of organic and inorganic compounds have potential to form a CT-complex whereas the common and popular dye sensitization always requires efficient dyes that are often costly and unstable. As we discussed in this review, various organic-inorganic compounds with diverse functional groups have been examined to make visible light active CT-complexes on TiO₂. In particular, CT-complexes with phenolic, hydroxyl, and carboxyl linkages have been much studied for the self-degradation of complexes themselves or for interfacial CT processes under visible light. The visible light activities of these CT-complexes have been demonstrated for both oxidative and reduction conversion processes. The TiO₂-H₂O₂ complex under visible light produces OH radicals which are strong oxidants that can be used for the mineralization of pollutants. TiO₂ complexes with cyanide (or isocyanate) generate quite stable photocurrent and can be used as a stable visible light photocatalyst. CT-complexation with TiO₂ is even possible through physisorption, which demonstrated visible light activity.

Although the general photoactivity of CT-complexes has not reached that of the dye-sensitized TiO₂ or UV-TiO₂ system, LMCT sensitization should be more widely investigated and developed to make it a more general and efficient method of visible light utilization. A majority of known examples are TiO₂-based systems but this LMCT-sensitization can be generalized to other semiconductor nanoparticles. Rajh *et al.*⁵⁰ reported that the surface modification of nanocrystalline ZrO₂ and Fe₂O₃ with enediol ligands (ascorbic acid, dopamine, alizarin) also induces a red-shift in the optical absorption compared to the unmodified nanocrystallites. These optical shifts are comparable to those obtained with TiO₂. The kinds of functional linkage groups, the degree of coupling between TiO₂ and a ligand, the HOMO level of a ligand, the crystalline structure and surface area of semiconductors, available electron acceptors, and pH are all important factors in influencing the formation of CT-complexes and their photoactivity.^{84-86,91,101} Therefore, modifications of the ligand structure and TiO₂ surface properties should induce significant changes in the photoactivity of the complex, which should be actively utilized to increase the overall solar conversion efficiency of LMCT sensitization.

Acknowledgements

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