Communication

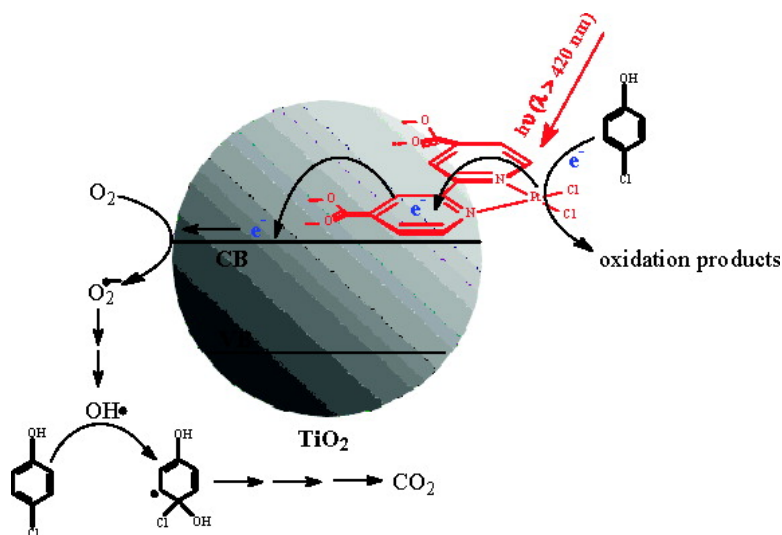# Visible-Light Induced Water Detoxification Catalyzed by Pt Dye Sensitized Titania

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Visible-Light Induced Water Detoxification Catalyzed by Pt[II] Dye Sensitized Titania

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Colloidal TiO_2 suspensions have proven to be excellent photo-catalytic materials on which many organic compounds are completely mineralized under ultraviolet band gap irradiation.[1,2] These materials have proven quite effective for the removal of toxic organic pollutants in wastewater and in the purification of drinking water.[1c,3] However, the sensitization of these photooxidation processes to visible light, essential for the application of terrestrial sunlight in emerging photocatalytic remediation technologies, has received far less attention.[4] While impurity doping[5,6] and dye sensitization[4] have been successfully applied to broadening the spectral response of TiO_2 in photocatalysis schemes, the latter approach generally necessitates the addition of undesirable sacrificial electron donors to promote regeneration of surface-bound sensitizer molecules. As dye sensitized systems solely rely on trapped conduction band electrons to reduce dioxygen to superoxide, eventually leading to the production of hydroxyl radicals (OH•), many dyes simply cannot withstand this severe oxidative stress. The present work identifies a highly stable photocatalytic material, $Pt(dcbpy)Cl_2/TiO_2$ (dcbpy = 4,4′-dicarboxy-2,2′-bipyridine), which promotes the visible-light sensitized ($\lambda > 420$ nm) decomposition of aqueous 4-chlorophenol (4-CP), a representative wastewater pollutant, in the presence of dioxygen without the need for sacrificial electron donors. Chemical additives are not required as the one electron oxidized form of $Pt(dcbpy)Cl_2$ ($E_{pa} > 735$ mV vs Fc^+/Fc) serves to irreversibly oxidize 4-CP itself ($E_{pa} = 525$ mV vs Fc^+/Fc), rendering two operable mechanisms assisting in its decomposition. Notably, the identical material using band gap excitation under inert atmospheric conditions in the presence of aqueous methanol serves as a photochemical precursor for highly efficient H_2 evolving Pt nanoparticles on the surface of TiO_2.[7]

Photocatalytic materials containing varying amounts of $Pt(dcbpy)_2Cl_2$ by mass on Degussa P-25 TiO_2 were prepared using the same basic aqueous media adsorption procedure we described previously;[7] see Supporting Information for details. To test photocatalytic activity, the photoinduced conversion of 4-CP was carried out under visible light illumination (300 W Xe lamp equipped with both water and 420 nm long pass filters) on aqueous $Pt(dcbpy)Cl_2/TiO_2$ dispersions. The data displayed in Figure 1 clearly indicate that under identical reaction conditions all $Pt(dcbpy)Cl_2/TiO_2$ samples exhibit significant activity for the decomposition of 4-CP as monitored by UV−vis spectroscopy. In the 2 wt % $Pt(dcbpy)Cl_2/TiO_2$ system, ∼90% of 4-CP is decomposed after 6 h of irradiation in aerated solution, while no significant degradation occurs on pure TiO_2. The fact that an aqueous solution of $Pt(dcbpy)Cl_2$ and 4-CP induces no degradation of the chemical under visible light irradiation eliminates the possibility that decomposition of 4-CP was initiated by a photoreaction with the excited state of $Pt(dcbpy)Cl_2$. Given the excited-state lifetime of the analogous diethylester compound is 8.7 ps,[8] bimolecular electron transfer chemistry here is diffusionally impossible and the lack of
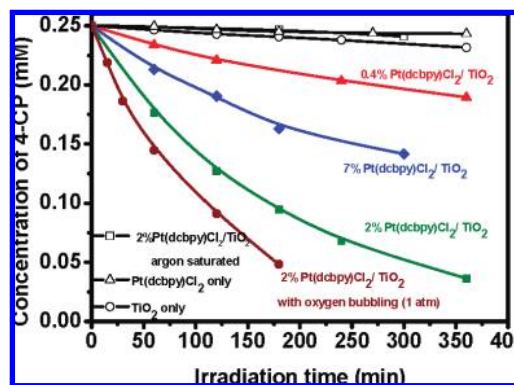

Figure 1. Temporal course of the photodegradation of 4-CP (2.5×10^{-4} M; 50 mL total volume) in aqueous dispersions at pH 7.0 containing 50 mg of catalytic materials under visible light irradiation ($\lambda > 420$ nm).

reactivity in the control experiment comes as no surprise. It is clear that TiO_2 is necessary for the reactions to proceed; it provides the reaction surface for the adsorbed molecules, serves as the electron carrier/mediator, and facilitates electron transfer between adsorbed components.[1−4] We note that O_2 is also an essential component which generates a variety of free radicals in the presence of trapped conduction band electrons, promoting oxidation of 4-CP.[1c,9] In the absence of O_2, 4-CP is not degraded with visible light in the 2% $Pt(dcbpy)Cl_2/TiO_2$ system, whereas the presence of 1 atm of O_2 accelerates 4-CP decomposition, Figure 1. The former result suggests that charge recombination between the conduction band electron and oxidized sensitizer outcompetes potential reactions of 4-CP with the latter. We postulate that when trapped conduction band electrons are consumed in radical forming reactions, this gives the oxidized dye additional time for electron transfer with 4-CP, thus enabling a second decomposition mechanism.[6] The combined experimental results indicate that the presence of three components (Pt^{II} complex, TiO_2 and O_2) is essential to drive the photocatalysis. A series of $Pt(dcbpy)Cl_2/TiO_2$ samples containing $Pt(dcbpy)Cl_2$ from 0.4 to 7.0 wt % were examined, and an optimum value of 2% was found, Figure 1. This can be attributed to the fact that a compromise must be attained between TiO_2-adsorbed reaction components;[4c] the presence of too much $Pt(dcbpy)Cl_2$ hinders the adsorption of 4-CP and vise-versa, leading to lower catalytic activities on the extremes.

The mechanism of photodegradation mediated by TiO_2 under visible light irradiation largely involves the generation of OH• radicals, as illustrated in the Table of Contents graphic.[1c,6,9,10] To confirm the formation of OH• in the current system, three independent radical trapping experiments were performed on optimized photocatalytic mixtures, and in each case OH• radicals were detected. While the hydroxylation of benzoic acid is routinely used as an indicator for OH• radicals[11] and was indeed successful
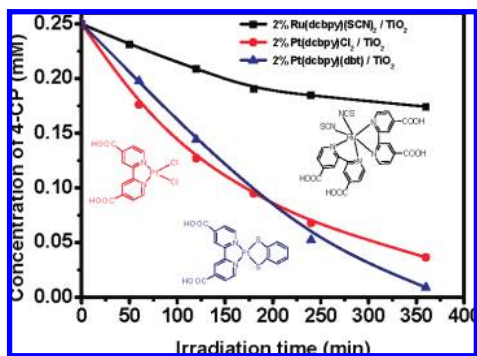
Figure 2. Temporal course of the photodegradation of 4-CP (2.5×10^{-4} M; 50 mL) in aqueous dispersions at pH 7.0 containing 50 mg of catalytic materials under visible light irradiation ($\lambda > 420$ nm).

here, more definitive proof emerges from the OH$^{\bullet}$-radical specific, dose-dependent optical probe HPF[12] in addition to EPR spin trapping experiments with DMPO,[5b] Figures S1−S5. These combined results support the notion that OH$^{\bullet}$ radicals are indeed formed through the proposed O_2 reduction pathway and is in agreement with data obtained previously on Pt^{IV}-doped titania materials.[6]

To monitor the stability of the Pt^{II} dye photocatalyst, the complex was removed from representative photolyzed and unphotolyzed TiO_2 samples and their UV−vis spectra were compared, Figure S6. After 6 h of reaction, no decomposition of Pt(dcbpy)Cl_2 was detected under the experimental conditions of Figure 1. However, the combination of a higher initial concentration of 4-CP (1 mM) and 24 h of continuous photolysis rendered ∼6% of the Pt-(dcbpy)Cl_2 either desorbed from the TiO_2 during the photocatalysis or consumed in an unspecified reaction. These results do in fact demonstrate that this complex is regenerated either through direct oxidation of the 4-CP or from its associated oxidation products. The current strategy is rather unique as it incorporates the 4-CP pollutant as the "sacrificial donor" which could potentially be harnessed for exploitation in photochemical energy production. To monitor the complete destruction of 4-CP using the present materials, CO_2 formation, the ultimate carbon-based oxidation product, was monitored online by GC analysis, Figure S7. Complete mineralization of 4-CP is indeed realized using the current Pt^{II} dye sensitized titania nanomaterials.

To investigate the generality of using Pt^{II} complex sensitizers in photooxidation processes on TiO_2, Pt(dcbpy)(bdt), bdt = 1,2-benzenedithiolate, was synthesized[13] and subjected to the same reaction conditions as those described above. The experimental results clearly indicate that the 4-CP is decomposed with visible light (Figure 2), demonstrating that the degradation process is indeed initiated through electron transfer from the excited state of the Pt^{II} complex to the conduction band of TiO_2. However, unlike Pt-(dcbpy)Cl_2, Pt(dcbpy)(bdt) is completely decolorized over the course of the reaction as it cannot withstand the oxidative stress afforded in the reaction mixture. The relevant potential of Pt(dcbpy)(bdt), $E_{pa} = 486$ mV, is not favorable for the oxidation of 4-CP, resulting in inefficient regeneration of the dye following charge injection. The oxidized dye is then subject to decomposition which results in its decolorization.

cis-Ru(dcbpy)$_2$(NCS)$_2$ is among the best photosensitizers used in mesoporous TiO_2-based dye sensitized solar cells (DSSCs).[14] To probe the possibility that it might serve as a photosensitizer to promote oxidation chemistry, this complex was prepared[14b] and anchored to the surface of TiO_2. As shown in Figure 2, this Ru^{II} dye inefficiently drives 4-CP oxidation and also degrades with

photolysis time, Figure S8. This particular case deserves further consideration as it represents a potentially relevant decomposition pathway for cis-Ru(dcbpy)$_2$(NCS)$_2$ in operational DSSCs.

In summary, a new dye sensitization system incorporating Pt(dcbpy)Cl_2 on titania for the photodegradation of aqueous organic pollutants under visible light irradiation has been realized. The experimental results suggest that injected conduction band electrons initiate the reduction of dioxygen which promotes hydroxyl radical formation. The presence of OH$^{\bullet}$ radicals in the present system was verified by three independent scavenging experiments. The hydroxyl radicals produced from the reductive route leads to the photooxidation of 4-CP along several concurrent reaction pathways, leading to rapid decarboxylation and dechlorination.[1c,9] Given the positive oxidation peak potential exhibited by Pt(dcbpy)Cl_2 in this study, 4-CP is thermodynamically poised for irreversible oxidation by these surface bound structures, opening a second oxidative degradation pathway. The experimental data support 4-CP serving the role of sacrificial electron donor which regenerates the resting oxidation state of the Pt^{II} dye sensitizer. We believe the general concept of using organic pollutant rich wastewaters in solar hydrogen generation schemes will be relevant for large scale photochemical energy production utilizing molecular charge transfer complexes.

Supporting Information Available: Experimental details, radical trapping experiments, and CO_2 production data. This material is available free of charge via the Internet at http://pubs.acs.org.

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