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Multi-Electron Transfer from Heme-Functionalized Nanocrystalline TiO_2 to Organohalide Pollutants

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A significant challenge in the photochemical sciences is to identify assemblies that can store and transfer multiple electrons to a substrate when illuminated with light. Multi-electron transfer (MET) processes avoid high-energy free radical intermediates and can yield desired reaction products under mild conditions. The synthesis of chromophoric molecular compounds capable of MET is challenging, although some notable breakthroughs have recently been realized.[1−3] Nanomaterials, on the other hand, that can harvest solar energy and store multiple electrons are easily synthesized but often lack the selectivity of molecular catalysts.[4,5] Herein, we describe a new and broadly applicable approach for photodriven molecular MET catalysis. Well-defined molecular catalysts (hemes) anchored to mesoporous nanocrystalline (anatase TiO_2) thin films were found to trap, store, and transfer multiple electrons to organohalide pollutants. Each nanoparticle was found to store >500 reducing equivalents upon illumination. A notable synergy between the molecular catalysts and the semiconductor was observed.

Mesoporous nanocrystalline TiO_2 films were prepared by the hydrolysis of $Ti(i\text{-}OPr)_4$ by a sol−gel method previously described in the literature.[7] Anatase TiO_2 nanoparticles prepared in this manner were ∼15 nm in diameter, and the film thickness was ∼10 μm. Hemin (Fluka) was attached to nanocrystalline TiO_2 films from micromolar DMSO solutions at room temperature. Hemin (protoporphyrin IX chloride)-functionalized TiO_2 films were immersed in solutions of neat methanol or, in some cases, aqueous solutions of 6.7×10^{-4} M acetic acid (pH = 4) or 0.1 M sodium citrate (pH = 8) and were purged with N_2. Band gap excitation resulted in the reduction of hemin to heme, and continued photolysis led to the appearance of the well-known absorption of TiO_2 electrons ($TiO_2(e^-)$) that absorb light throughout the visible and into the infrared region.[8] Valence band holes are known to irreversibly oxidize methanol (or carboxylates) that allows the concentration of $TiO_2(e^-)$ to build up under steady-state photolysis.[5,9] Under the experimental conditions investigated, we estimate that each TiO_2 nanoparticle contains on average ∼50 hemes and 600 $TiO_2(e^-)$.[8] Concentrations of $TiO_2(e^-)$ could be controlled by photolysis time, and the heme surface coverage could be independently tuned through equilibrium binding.[10]

The photogenerated hemes and $TiO_2(e^-)$ were stable under anaerobic conditions for several days. Organohalide (RX) pollutants trichloroethylene (TCE), 1,2-dichlorobenzene, 1-bromobenzene, and 1-chlorobenzene introduced to the external solutions were found to initiate redox reactivity. The experiments were performed in the dark to preclude secondary photolytic reactions. Figure 1 shows the change in absorbance with time after 1,2-dichlorobenzene was added to the external solvent. The spectral changes observed were qualitatively similar for all the organohalides investigated. The concentration of $TiO_2(e^-)$ decreased rapidly to less than 10% of the initial value, after which time the heme was oxidized to hemin (inset Figure 1). The first-order rate constants for the appearance of oxidized heme (hemin) and the loss of heme were, within experimental error, the same. At long reaction times, the initial hemin/TiO_2 absorption spectrum was observed, consistent with quantitative reactivity based on heme. The spectral changes are consistent with at least two mechanistic pathways: (1) a heme-mediated reduction; or (2) reduction first by $TiO_2(e^-)$ and then by heme/TiO_2. The first pathway requires that the $TiO_2(e^-) \rightarrow Fe(III)$ charge transfer be faster than $Fe(II) \rightarrow RX$. The latter pathway requires rapid reduction of RX by the $TiO_2(e^-)$.

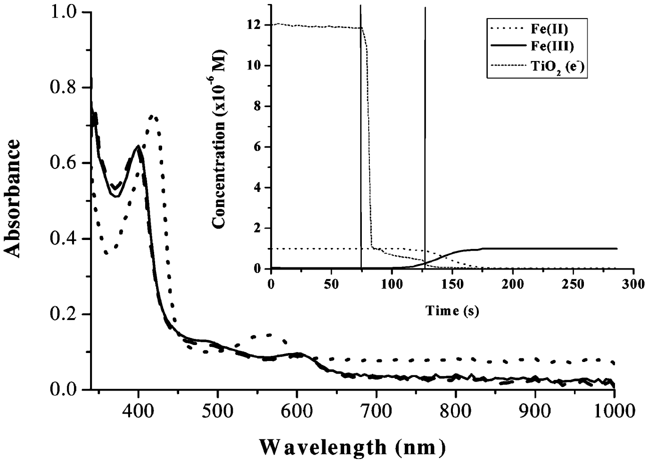

Figure 1. UV−visible absorbance spectra of hemin/TiO_2 (- - -), after photolysis: heme/$TiO_2(e^-)$ (• • •), and after addition of 1,2-dichlorobenzene to yield hemin/TiO_2 (—). The inset shows time-resolved concentration changes upon addition of RX. The first vertical line indicates the time of RX injection (75 s), and the second line corresponds to the time when >90% of the $TiO_2(e^-)$ was consumed and heme oxidation begins.

Comparative studies with titanium dioxide electrons in the absence of heme and heme alone were investigated. Heme is a naturally occurring porphyrin that is known to reduce a variety of alkyl halides[11] but was unreactive toward TCE or the arylhalides in methanol. The $TiO_2(e^-)$s showed measurable reactivity with the arylhalides but none with TCE. Figure 2 shows that the concentration of $TiO_2(e^-)$ decreased to near zero within 20 s upon addition of 1,2′-dichlorobenzene when heme was anchored to the semiconductor surface. In contrast, under the same conditions, the $TiO_2(e^-)$ decreased by only about half after 30 min in the absence of heme. Both reactions were found to be first-order in aryl halide. In general, the second-order rate constants for aryl halide reduction by $TiO_2(e^-)$ was 80−150 times larger in the presence of heme (Table 1). Such data are most consistent with heme-mediated RX reduction and suggest cooperativity between hemes and the semiconductor conduction band electrons. We note that there was no spectroscopic evidence for RX adsorption to TiO_2 or to hemin-functionalized TiO_2 in the dark.

Neither $TiO_2(e^-)$ nor heme alone showed measurable reactivity with TCE after 3 days. However, the reaction proceeded rapidly

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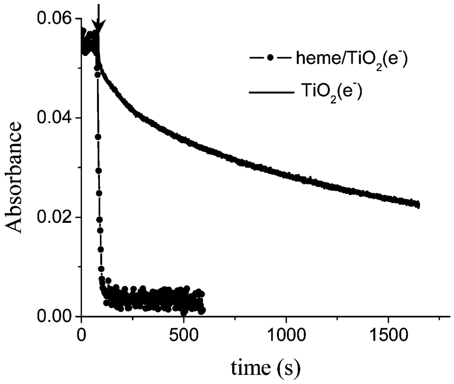
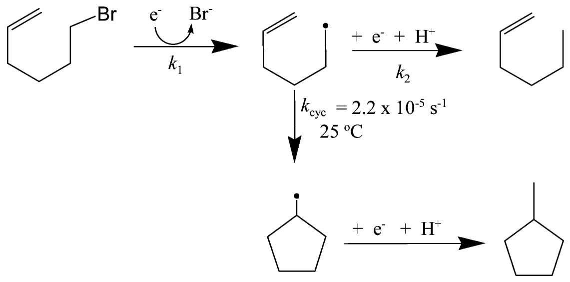


Figure 2. Absorbance at 1000 nm of heme/TiO$_2$(e$^-$) (• • •) and TiO$_2$(e$^-$) (—) as a function of time. The arrow indicates the point at which 1,2-dichlorobenzene was added to the external methanol solution.

Table 1. Rate Constants for Organohalide Reduction by TiO$_2$(e$^-$) and Heme/TiO$_2$(e$^-$) in Methanol

organohalide	TiO$_2$(e$^-$) k (M^{-1} s^{-1})	heme/TiO$_2$(e$^-$) k (M^{-1} s^{-1})
bromobenzene	0.43 ± 0.04	36.47 ± 1.10
chlorobenzene	0.050 ± 0.006	3.78 ± 0.13
dichlorobenzene	0.070 ± 0.002	10.42 ± 0.27
trichloroethylene	No Rxn.	0.76 ± 0.03

Scheme 1



for heme/TiO$_2$(e$^-$) in methanol (Table 1), and at pH 8, $k = 0.22 \pm 0.02$ m^{-1} s^{-1}. A possible explanation for this is that the first reduction potential of TCE is too negative, $E° = -0.69 \pm 0.01$ V, and the reduction occurs by the more thermodynamically favorable two-electron pathway, $E° = +0.52 \pm 0.01$ V vs NHE.[12]

This possibility was further investigated with radical clocks that yield characteristic products from one- and two- electron transfer reactions.[13] As shown in Scheme 1, 6-bromo-1-hexene yields 1-methylcyclopentane through two single-electron transfer reactions, while a rapid two-electron transfer produces 1-hexene. Reactions of 6-bromo-1-hexene with TiO$_2$(e$^-$) and heme/TiO$_2$(e$^-$) were analyzed by GC−MS. 1-Methylcyclopentane was the sole product observed for TiO$_2$(e$^-$). For reactions of 6-bromo-1-hexene with heme/TiO$_2$(e$^-$), both 1-hexene and 1-methylcyclopentane were formed in relative yields of 69 ± 5 and 31 ± 5%, respectively. The formation of 1-hexene indicates that the second electron was transferred to RX at a rate faster than that of the free-radical cyclization reaction. In other words, the heme/TiO$_2$(e$^-$) nanocrystallites delivered two electrons to RX within 4.5 μs.

In summary, we have quantified the kinetics for TCE and aryl halide reduction by hemes anchored to TiO$_2$(e$^-$). It is noteworthy that these same reactions are not observed for hemes in fluid solution and do not occur, or are much slower, for TiO$_2$(e$^-$)s alone under otherwise similar conditions. Radical clock studies clearly demonstrate that rapid microsecond multi-electron transfer reduction occurs at the heme/TiO$_2$ interface. The semiconducting nature of the mesoporous TiO$_2$ thin films allows the reactive states to be controlled with light and/or applied potential,[10,14] behavior that is difficult, if not impossible, to achieve with colloidal solutions.[15] In principle, the relative concentrations of conduction band electrons and hemes can be systematically tuned to yield desired reaction products. We emphasize also that the approach here is not limited to naturally occurring heme catalysts or to TiO$_2$ and can be extended to a wide variety of naturally occurring or synthetic catalysts and nanomaterials for other environmental or catalytic applications. Future studies of heme/TiO$_2$(e$^-$) will focus on the mechanistic details for multi-electron transfer as well as identification of the RX reduction products.

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