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Titanium Dioxide Visible Light Photocatalysis: Surface Association Enables Photocatalysis with Visible Light Irradiation

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Abstract

Titanium dioxide (TiO₂) is a widely employed and inexpensive photocatalyst, but its use in organic synthesis has been limited by the short-wavelength ultraviolet irradiation typically used. We have discovered that TiO₂ particles efficiently mediate photocatalytic radical cation Diels-Alder cycloadditions using a simple visible light source, enabled by the formation of a visible light absorbing complex of the substrate on the semiconductor surface.

Graphical Abstract

Titanium dioxide is an inexpensive white pigment employed in many consumer and industrial applications. As a semiconductor, TiO₂ possesses a band gap of ~3.1 eV; i.e., TiO₂ does not absorb light in the visible region (400–700 nm). The photocatalytic activity of TiO₂ usually requires UV excitation to promote an electron from the valence band (VB) to the conduction band (CB), generating a short-lived electron-hole pair that can participate in reductive (electron, e⁻) or oxidative (hole, h⁺) processes, as illustrated in Figure 1.¹

As part of ongoing studies of photocatalytic activity of TiO₂ in a variety of organic transformations, we tested the Diels-Alder reaction of indole with 1,3-cyclohexadiene.² Much to our surprise, an aerated sample of TiO₂, indole, 1,3-cyclohexadiene, acetyl chloride and NaHCO₃ in nitromethane irradiated for 5 h using a blue LED centered at 460 nm gave the desired [4+2] product in 60% yield (Scheme 1, see ESI for experimental conditions). Indole, TiO₂, and the other reaction components show no absorption at this wavelength; in fact, their absorptions are well into the UV region (*vide infra*). Importantly, a control

experiment performed in the absence of TiO_2 displayed no reactivity, confirming that the reaction was not occurring through direct photosensitization of the reagents (see ESI).

The observation of visible light photochemistry using TiO_2 is exciting because it could increase the potential utility of this photocatalyst in organic synthesis. At first glance, this result appears to violate the first law of photochemistry, which simply states that light must be absorbed in order to promote chemical change.³ Herein, we present studies investigating the origin of this unexpected result. We have found that while the individual reaction components do not absorb at 460 nm, a surface interaction between the TiO_2 semiconductor and indole produces a new, weak absorption band that is crucial in promoting the photocatalytic Diels-Alder reaction. We hope that a deeper understanding of the physical organic chemistry enabling the visible light photochemistry of TiO_2 may prove to be enabling in many other synthetically useful photoredox transformations.

As the scope of photoredox transformations expands and finds more applications in organic chemistry⁴, the understanding of the spectroscopic and mechanistic aspects that underlie these studies has become increasingly important.⁵ In this contribution, we investigate in detail why a reaction with unfunctionalized TiO_2 works at 460 nm. In the process, we illustrate the strategies that can be implemented to resolve mechanistic issues such as the one discovered here. The rationalization of this observation provides a simple strategy to perform photocatalytic Diels-Alder cycloadditions with visible light under mild conditions; further, the strategy is likely applicable to other reactions that may involve substrate-surface interactions.

In order to investigate this phenomenon further, we first examined the effect of indole on the absorption spectrum of the TiO_2 photocatalyst. It has been proposed that amines can associate to the surface of TiO_2 , which can facilitate the single electron oxidation of the amine.⁶ In 2015, Chen and coworkers observed charge-transfer interactions between TiO_2 and benzylamine that resulted in approximately 20 nm shift of the TiO_2 band edge.⁷ By use of a sharp long pass filter at 400 nm they were able to show that part of the visible light from a xenon lamp could promote aerobic benzylamine and sulfide oxidations. Therefore, we hypothesized that indole might be engaging in a similar association with TiO_2 and that perhaps this interaction was responsible for a new absorption in the visible region. Thus, we performed two diffuse reflectance measurements, one with TiO_2 that was exposed to MeNO_2 , and a second measurement in which the TiO_2 sample was exposed to a solution of indole in MeNO_2 . The results of these measurements are presented in Figure 2(B). We did not observe a change in the absorption of TiO_2 in the presence of MeNO_2 alone; however, in the presence of the solution of indole, the formation of a new weak absorption in the visible region was observed, which extended to 520 nm. These results are also consistent with the characterization of TiO_2 which was recovered by centrifugation after the reaction (see ESI).

To confirm that formation of the absorption band was occurring due to the association of indole to the TiO_2 surface, we performed FTIR analysis on a sample of TiO_2 that had been exposed to a 0.1 M solution of indole, the same concentration employed under standard reaction conditions. As seen in Figure 3, the TiO_2 -indole sample contained bands characteristic of indole, while the sample of pure TiO_2 contained no bands in this region.

Interestingly, the band corresponding to the N-H stretch of indole was not present in the TiO₂-indole sample (see ESI). These results are consistent with previous studies by Busca and coworkers, who observed similar IR spectral features when indole was combined with other metal oxides such as zirconia and alumina.⁸ From these data, they concluded that the adsorption of indole onto the surface of metal oxides is dissociative. Due to the lack of an observable indole N-H stretch band in the presence of TiO₂, we propose a similar type of interaction.

In order to test if the absorption of this complex was responsible for the observed Diels–Alder reactivity, we decided to obtain an action spectrum. An action spectrum can be described as a plot of the apparent quantum yield of the reaction versus the wavelength of incident photons.⁹ An action spectrum can be used to help differentiate if the photoreaction is simply the consequence of a lowering of the semiconductor band gap, which in our case is by ~8 nm (see Figure 2B), or due to the weak interaction leading to a band that extends to longer wavelengths (ca. 520 nm in our case). If the mechanism only involves excitation of TiO₂ (sometimes referred as *direct photocatalysis*), the action spectrum would simply resemble the absorption profile of the photocatalyst. If, however, the mechanism requires excitation of the weak complex (sometimes referred as *indirect photocatalysis*), then the action spectrum would resemble the absorption profile of the TiO₂-indole complex.

In order to construct an action spectrum, four experiments were performed, irradiating with LEDs of varying wavelengths (405 nm, 460 nm, 500 nm and 520 nm). The results of each experiment after 2 h of irradiation are displayed in Table 1.

In order to simplify the calculations for the apparent quantum yields, each LED was set to an irradiance of 30 W/m². The energy of a photon at each wavelength can be defined as equations 1 and 2, where h is Planck's constant (6.626×10^{-34} J·s or W·s²), c is the speed of light (2.998×10^8 m/s), and λ is the wavelength of the light source in nm.

$$E_{\text{ph}} = h \times (c/\lambda) \quad (1)$$

$$E_{\text{ph}} \text{ (in kcal/mol)} = 28,600/\lambda \text{ (in nm)} \quad (2)$$

From this relationship, the number of photons arriving at the sample can be determined from the irradiance. Dividing this value by Avogadro's number gives the photon flux, or the moles of photons (i.e., einsteins) arriving at the sample per unit time, resulting in equation 3.

$$\Phi = \frac{(30 \text{ W m}^{-2})(\lambda)/(h)(c)}{(6.022 \times 10^{23} \text{ mol}^{-1})} \quad (3)$$

The photon flux was calculated for each LED used, and the initial rate was corrected by the photon flux for each experiment to obtain the apparent quantum yield (Table 1). Finally, an action spectrum can be obtained by plotting the apparent quantum yield (ν_0/Φ) versus the wavelength of the incident photons.

In order to determine the nature of the mechanism of the photocatalytic Diels-Alder reaction, the action spectrum was compared to both the diffuse reflectance spectrum of the TiO_2 catalyst and the absorption spectrum of the TiO_2 -indole complex. As demonstrated by Figure 3(A), it is unlikely that the photocatalytic Diels-Alder reaction is proceeding through direct band gap excitation, as we would expect that only the reaction performed at 405 nm would yield reactivity in that case. However, when the action spectrum is compared to the absorption spectrum of the TiO_2 -indole complex, as seen in Figure 3B, an almost perfect correlation between the two spectra is observed. This is compelling evidence that excitation of the complex is an integral step in initiating the photocatalytic Diels-Alder reaction.

Based on these data, we propose the mechanism for the photocatalytic reaction presented in Figure 4. Indole first associates to the surface of TiO_2 , giving rise to an absorption band that extends into the visible region. The adsorption of indole is proposed to be dissociative, similar to the behaviour observed with other metal oxides.⁸ This complex can then be excited by a 460 nm LED light source, resulting in the injection of an electron into the CB of TiO_2 . In order to prevent back-electron transfer, the electron in the CB ($E_{1/2} = -2.0$ V vs. SCE)¹⁰ is quenched by either MeNO_2 ($E_{1/2} = -0.91$ V vs. SCE)¹¹ or O_2 ($E_{1/2} = -0.73$ V vs. SCE).¹² Upon forming the indole radical-cation, it can then undergo a [4+2] radical cyclization with 1,3-cyclohexadiene. We note that the radical cation in blue in Figure 4 is drawn as independent of the TiO_2 surface; however, our experiments cannot differentiate between a radical-cation that has been released or remains with some affinity for the surface. After cyclization, an electron from the CB of TiO_2 can then reduce the tetrahydrocarbazole radical-cation. It may also be possible that the radical-cation could oxidize another indole molecule, creating a propagating chain; however we have not investigated this possibility in detail. Finally, the tetrahydrocarbazole is rapidly acylated in order to protect it from oxidation, as the corresponding tetrahydrocarbazole has a lower oxidation potential ($E_{1/2} = 0.46$ vs SCE) compared to the starting material, indole ($E_{1/2} = 1.07$ V vs. SCE).²

In conclusion, the observation of a photoactive complex between indole and TiO_2 leads to visible light photochemistry in a system where all reaction participants do not absorb light in this region. In our case it is clear that it is not the small shift in the semiconductor band edge, but rather the absorption of the newly formed complex that is responsible for the photochemistry observed. This could potentially be a general phenomenon for electron rich molecules with available n -electrons. We hope that our detailed spectroscopic study will inspire others to explore visible light photochemistry in systems that may appear to violate the first law of photochemistry.³ The Natural Sciences and Engineering Research Council of Canada supported this work through its Discovery and graduate scholarships programs. Thanks are due to the Canada Research Chairs program for an award to J.C.S.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

UVA excitation of TiO₂ generates an electron-hole pair that mediates redox photocatalysis (A: electron acceptor; D: electron donor). Visible light (>400 nm) is not absorbed by TiO₂.

Figure 2.

(A) Absorption spectra for the reaction components for the photocatalytic Diels-Alder reaction with unfunctionalized TiO_2 . The absorbance scale on the left applies to a solution of indole (95 mM), while the reflectance scale on the right applies to solid TiO_2 . (B) Effect on the absorption of TiO_2 in the presence of indole. Inset: Zoomed region displaying the formation of a new absorption band.

Figure 3. FTIR spectra of (A) pure indole, (B) TiO₂ (blue) and TiO₂ that was exposed to a 100 mM solution of indole (red).

Figure 4. Comparison of the acquired action spectrum with (A) the diffuse reflectance spectrum of the TiO_2 photocatalyst, and (B) with the absorption of the TiO_2 -indole complex.

Figure 5.
Proposed mechanism for the photocatalytic Diels-Alder reaction between indole and 1,3-cyclohexadiene.

Scheme 1.

The heterogeneous TiO_2 -catalyzed photochemical Diels-Alder reaction between indole and 1,3-cyclohexadiene.

Table 1

Experimental and calculated data for the construction of an action spectrum

LED Wavelength	Yield	ν_0 (mol/min)	Φ (mol/m ² min)	ν_0/Φ
405 nm	40%	1.00×10^{-6}	6.09×10^{-3}	1.64×10^{-4}
460 nm	35%	8.75×10^{-7}	6.91×10^{-3}	1.27×10^{-4}
500 nm	26%	6.50×10^{-7}	7.52×10^{-3}	8.64×10^{-5}
520 nm	28%	7.00×10^{-7}	7.82×10^{-3}	8.95×10^{-5}

Reaction Conditions: Indole (0.3 mmol), 1,3-CHD (1.5 mmol), acetyl chloride (0.3 mmol), NaHCO₃ (0.6 mmol), TiO₂ (12 mg), and MeNO₂ (3 mL) were placed in a 10 mL Schlenk tube and irradiated for 2 h under air using a LED light source set at 30 W/m². Yields are reported based on ¹H NMR using trimethyl(phenyl)silane as an external standard.