The Role of Ruthenium Photosensitizers in the Degradation of Phenazopyridine with TiO₂ Electrospun Fibers

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Abstract

There has been increased interest in titanium dioxide (TiO₂) fibers as a photocatalyst for the degradation of persistent organic and biopharmaceutical toxins in the environment. The photocatalytic efficiency of TiO₂ fibers is typically limited to UV irradiation due to its semiconductor bandgap. TiO₂ fibers have been prepared and adsorbed the visible photosensitizer *cis*-dichlorobis(2,2'-bipyridyl-4,4'-dicarboxylic acid)ruthenium (II) (Ru(dcbpyH₂)₂Cl₂) on the surface in order to absorb from 300-800 nm in the visible spectrum and drive photocatalysis. This dye fiber material has been applied to the degradation of 2,6-pyridinediamine,3-(phenylazo) monohydrochloride or phenazopyridine (PAP) as a model biopharmaceutical waste. The Ru(dcbpyH₂)₂Cl₂-sensitized fibers degrade PAP under UV and visible irradiation following a first order reaction rate. The rate constants for PAP degradation in visible light showed very little change from $0.011 \pm 0.002 \text{ min}^{-1}$ to $0.014 \pm 0.001 \text{ min}^{-1}$ in the presence of the dye fiber material. Under UV irradiation, the rate decreased from $0.032 \pm 0.003 \text{ min}^{-1}$ and $0.012 \pm 0.002 \text{ min}^{-1}$. These results suggest that the major pathway for the degradation of PAP may occur through the valence band.

Keywords: Dye sensitization; TiO₂; Electrospun fibers; Photodegradation; Phenazopyridine

Introduction

Semiconducting oxides are a promising class of materials for the photodegradation of organic pollutants.¹⁻⁵ Titanium dioxide (TiO₂) has been thoroughly investigated as a photooxidizer that is stable, low cost, and environmentally friendly. However, its wide band gap (~3.0 eV) requires UV radiation, which is not optimal for environmental applications,

particularly in remote settings, that rely on visible solar radiation. In order for TiO_2 to be more feasible photocatalyst, it must be able to absorb more of the solar spectrum in the visible and near IR irradiation from 400-800 nm, making up 43% and 52% of the solar spectrum respectively. To improve the effectiveness of these photocatalysts in the visible region, TiO_2 can be modified with metal nanoparticle loading, metal ion doping, dye sensitization, composite semiconductor and anion doping.²⁻⁶ One issue with doping is the introduction of trap sites decreases the efficiency of the electron/hole transfer to the surface, reducing the number of radicals present in solution.² For this reason, our focus is to modify the surface to expand the region of absorption into that commonly used in dye sensitized solar cells (DSSCs).⁷

Ruthenium polypyridyl complexes are common sensitizers used in TiO_2 based DSSCs due to their strong visible absorption and efficient electron injection into semiconductor layers.⁷⁻¹² Here, the dye studied was *cis*-dichlorobis(2,2'-bipyridyl-4,4'-dicarboxylic acid)ruthenium (II) ($\text{Ru}(\text{dcbpyH}_2)_2\text{Cl}_2$), shown in Figure 1a. The dye is a strong electron injector due to of the covalent interactions with the metal oxide through the carboxylic acid anchoring groups and the close energy of the LUMO compared to the conduction band of TiO_2 as shown in Figure 1b, resulting in electron injection rates on the sub-picosecond timescale.¹³⁻¹⁵

Figure 1: a) Molecular structure of $\text{Ru}(\text{dcbpyH}_2)_2\text{Cl}_2$. b) Energy level diagram for TiO_2 and $\text{Ru}(\text{dcbpyH}_2)_2\text{Cl}_2$.

Our group has previously studied the degradation of the biopharmaceutical pyridinediamine,3-(phenylazo) monohydrochloride, or phenazopyridine (PAP), shown in Figure 2. PAP is commonly used as an analgesic and anesthetic drug to reduce pain from urinary tract infections, serves as a model pollutant due to its structural similarity to other known organic

toxins found in biomedical waste water.¹⁶ The presence of its azo-group, amines, and phenyl ring are similar to functional groups present on many toxic organic pollutants and other antibiotics like amoxicillin and tetracycline. These products can build up in biomedical waste streams and lead to contamination of environmental waters.¹⁶

Figure 2: Chemical structure of the environmental pollutant phenazopyridine.

Here we exhibit the feasibility of using TiO_2 as a photocatalyst under environmental conditions for the degradation of organic pollutants by expanding the dye sensitized absorption into the visible region. This was accomplished using the same concept as DSSCs using a dye as a photosensitizer, injecting electrons into the electron conducting TiO_2 layer as shown in Figure 3. Cis-dichlorobis(2,2'-bipyridyl-4,4'-dicarboxylic acid)ruthenium(II) is a known electron injecting dye that will be used to sensitize TiO_2 electrospun fibers. Prior studies have shown that excited electrons in the conduction band favor the formation of peroxide radical anions in the presence of adsorbed oxygen on the surface.¹⁷ The generation of these radicals in the presence of visible light is expected to improve the effectiveness of the catalyst, increasing the rate of PAP degradation.

Figure 3: The absorption of a photon promotes the excitation and injection of an electron for the photosensitizer to the semiconductor.

Experimental methods

Materials

All materials were purchased commercially and used as received unless otherwise indicated. Poly(methyl methacrylate) (PMMA), 4,4-dimethyl-2,2'-bipyridine, $\text{RuCl}_3(\text{H}_2\text{O})_3$, titanium isopropoxide (TTIP), anhydrous dimethylformamide (DMF), and ethanol were purchased from Sigma-Aldrich. Chloroform, diethyl ether, acetone, and sodium dichromate were purchased from Fisher. The solvents hydrochloric acid and sulfuric acid were purchased from JT Baker. Cis-dichlorobis(2,2'-bipyridyl-4,4'-dicarboxylic acid)ruthenium(II) ($\text{Ru}(\text{dcbpyH}_2)_2(\text{Cl})_2$) was synthesized using a procedure from the literature under nitrogen and was used without further purification.¹⁸ Reactions that were light sensitive were conducted in the dark and the reaction apparatus was covered with aluminum foil.

Characterization

The pre-calcined TiO_2 polymer fibers were fabricated using a high voltage Spellman SL 30 generator. The photodegradation experiments were performed using an Oriel 66001 UV lamp (100-400 nm range) with Oriel 68805 40-200 Watt universal Arc lamp power supply. UV-Vis measurements of aliquots of PAP were made on a Hewlett Packard 8452A Diode Array spectrophotometer to track concentration change during the photodegradation experiment. Fourier transform infrared spectra (FTIR) of $\text{Ru}(\text{dcbpyH}_2)_2\text{Cl}_2$ and $\text{Ru}(\text{dcbpyH}_2)_2\text{Cl}_2$ -sensitized TiO_2 fibers were obtained using a Bruker Equinox 55. Scanning electron microscopy (SEM) images were obtained on a FESEM, Supra 55 VP from Zeiss. X-ray diffraction(XRD) of the calcined fibered was obtained using, PANalytical's X'Pert PRO Materials Research Diffractometer with $\text{Cu K}\alpha$ X-radiation ($\lambda = 1.5418 \text{ \AA}$).

Methods

Synthesis of TiO_2 Electrospun Fibers

TiO_2 fibers were prepared by a using a sol-gel synthesis, followed by electrospinning of polymer sol-gel, and calcination treatment of polymer fibers as shown in Scheme 1.^{17, 19, 20} A

polymeric sol-gel was generated by stirring and ambient hydrolysis of TTIP using 1:2 mass ratio of PMMA:TTIP, where 320 mg of PMMA (MW = 35,000 g/mol) was completely dissolved in 2 mL of chloroform followed by drop wise addition of 640 mg of TTIP with continuous stirring for 30 min. 2 mL of DMF was then added and stirred for 2 h to increase the dielectric constant of the composite solution which aids in the electrospinning process.

The high voltage (25 kV) pulled the precursor sol-gel from the syringe onto the conductive Al collector forming polymer fibers. The resulting polymer fibers were left overnight to allow for complete hydrolysis of TTIP to $\text{Ti}(\text{OH})_4$ and further condensation to amorphous TiO_2 followed by calcination treatment of 360°C for 4h to create mixed TiO_2 crystal phase fibers.

Preparation of $\text{Ru}(\text{dcbpyH}_2)_2(\text{Cl})_2$ - sensitized TiO_2 Fibers

0.7 mg of $\text{Ru}(\text{dcbpyH}_2)_2(\text{Cl})_2$ was added to 33.2 μL of 0.1 M NaOH solution, 20 mL of ethanol was added and the solution allowed to stir in the dark for ~ 0.5 h. To the solution, 12.2 mg TiO_2 fibers was added and stirred for 24 h. The resulting solution was washed with ethanol to remove any excess dye. For the washing process, the solution was centrifuged and the supernatant fluid was decanted and dried under vacuum.

Photodegradation Procedure

To a quartz vial or glass beaker, 12.0 mL of 144 μM PAP/water solution, 14.0 mg of photocatalyst (either TiO_2 fibers or $\text{Ru}(\text{dcbpyH}_2)_2\text{Cl}_2$ - sensitized fibers) was added. This solution was allowed to stir in the dark for 1 h. At 15 min time intervals, 1.0 mL aliquots were taken with a syringe during a 2 h time period. The 1.0 mL aliquot was centrifuged for 5 min and then 0.5 mL of the upper solution was obtained for concentration measurements using a UV-Vis diode array spectrophotometer. The remainder of the solution from the 1.0 mL aliquot was not put back into the reaction cell. The solution in the reaction cell was stirred in the dark for 1 h and irradiated with a UV lamp for another hour to perform degradation.

Results and Discussion

Electrospun TiO_2 fibers were prepared from a sol-gel precursor solution as described in the procedure and shown in Scheme 1. The solution was electrospun at 25 kV with an 11 cm

working distance from copper tip to aluminum collector. The fibers formed under these conditions at room temperature had an average diameter of 500 nm and a smooth morphology. The fibers were calcined at 360 °C for 4 hours under an ambient atmosphere to form crystalline TiO₂ fibers. These fibers were used as the control group for all subsequent testing. The preformed, calcined fibers were soaked in a 5.29 M Ru(dcbpyH₂)₂Cl₂ dye solution to promote binding of the dye at the surface of the fiber. Prior studies with derivatives of Ru(dcbpyH₂)₂Cl₂ have shown strong binding through the carboxylic acid function group to the surface of TiO₂ particles and thin films.²¹ All of the samples were allowed to dry prior to further studies.

Scheme 1: Schematic procedure for the process of the fabrication of the TiO₂ fibers and dye sensitized fibers including sol-gel preparation, electrospinning of polymer sol-gel solution, calcination treatment of polymer fibers, and soaking in dye solution.

SEM images were obtained of the electrospun TTIP polymer fibers, post-calcined TiO₂ fibers and the Ru(dcbpyH₂)₂Cl₂-TiO₂ sensitized fibers. Figure 4a shows an SEM image of TiO₂

polymer fibers after electrospinning the sol-gel solution. The fibers are long with a smooth surface morphology. The average diameter of the polymer fiber was approximately 500 nm. Figure 4b shows an SEM image of TiO₂ fibers after calcination. Compared to 4a, the fibers in 4b are shorter and more rod like with a folded surface morphology. The lengths of the fibers are shorter due to breakage during the calcination process. The loss of carbon from the PMMA polymer during calcination also results in a reduced average diameter to approximately 200 nm. Figure 4c shows the dye substituted TiO₂ to have a similar diameter and structure to those in 4b. However, there appears to be less of the folded morphology and a rougher surface morphology in this case.

Figure 4. SEM image of a) TiO₂ polymer fibers after electrospinning b) TiO₂ fibers after calcination at 360 °C for 4 hours under ambient atmosphere and c) Ru(dcbpyH₂)₂Cl₂-TiO₂ fibers.

X-ray Diffraction (XRD) was used to confirm the formation of post calcination crystalline TiO₂ fibers prior to adding dye. For the anatase phase, the major peaks were obtained at 2θ values of 25.2, 37.9, 48.1, 54.0, and 55.0° representing the Miller indices of (101), (004), (200), (105), and (211) planes, respectively. For the rutile phase, peaks were observed at 2θ values of 27.4, 36.1, 41.3, and 54.4°, respectively, representing the Miller indices of (110), (101), (111), and (211) planes, respectively. The weight fraction of anatase-to-rutile transformation in the post-calcined TiO₂ fibers can be calculated from the equation of $W_R = 1/[1+0.8(I_A/I_R)]$, where I_A is the X-ray integrated intensities of the (101) reflection of anatase at 2θ of 25.2° and I_R is that

of the (110) reflection of rutile at 2θ of 27.4° .^{22, 23} The TiO_2 fibers were determined to be 18% rutile based on the XRD in Figure 5. This anatase-to-rutile fraction was chosen because it is close to the fraction of Degussa P25 (25% rutile), which has been found to have better photocatalytic properties than pure anatase phase TiO_2 .²⁴

Figure 5: XRD data for post-calcined fibers showing an 18% rutile fraction. The solid vertical lines and dashed vertical lines represent pure anatase and rutile phase TiO_2 respectively.

FTIR spectroscopy was used to examine the binding of the $\text{Ru}(\text{dcbpyH}_2)_2\text{Cl}_2$ on the TiO_2 by comparing the pre and post soaked TiO_2 fibers shown in Figure 6. The splitting of the carbonyl peak in the dye at 1714 and 1605 cm^{-1} is a result of protonation and deprotonation of the carboxylic acid group on the dye. When looking at the dye bound to TiO_2 there are no peaks above 1700 cm^{-1} suggesting that only deprotonated dye is bound.²¹ There is an observed shift from the fibers at 1631 cm^{-1} to 1619 cm^{-1} in the dye sensitized fibers. This is in the region of the carboxylic acid group showing binding of the dye to the TiO_2 . The low intensity of the dye peaks in the dye-sensitized fibers is a result of a less than 1 wt.% loading of the dye on the fibers resulting in a weak signal.

Figure 6: IR spectrum for the dye, TiO₂ fibers, and dye soaked TiO₂ fibers.

Phenazopyridine Degradation

To explore the efficiency of the new materials as visible photocatalysts, degradations of PAP were conducted under both UV and visible irradiation in an aqueous solution. UV-Vis measurements were taken over time to monitor the changes in concentration of PAP. The dye sensitized fibers were compared to the control fibers, the dye, and samples with no catalyst under UV and visible irradiation to determine the role that the ruthenium dye plays in the degradation process of PAP.

Two controls and two experiments were conducted in duplicate. These experiments used a quartz cell which would allow UV irradiation to penetrate to the sample. The first control used PAP solution with no catalyst. The second control used a solution containing Ru(dcbpyH₂)₂Cl₂ and PAP. Experiments used bare TiO₂ fibers or Ru(dcbpyH₂)₂Cl₂ – sensitized TiO₂ fibers as a catalyst in a PAP solution within a quartz cell. The concentrations of PAP were tracked by measuring the absorbance over the course of 2 hours. The first hour (t = -60 to t = 0) of the experiment was conducted in the dark to allow the adsorption of PAP to equilibrate. This allowed for the stirring of the photocatalyst and PAP and thus adsorption of PAP molecules onto the surface of TiO₂.⁴ During the second hour of the experiment (t = 0 to t = 60), the sample was irradiated with a UV lamp. An aliquot of the solution was taken every 15 min which was

centrifuged to remove any suspended catalyst. The sample was taken from the centrifuged solution, and diluted with deionized water before absorbance measurements.

Under the experimental conditions stated above, the UV-Vis absorption spectrum of the PAP degradation using TiO_2 fibers and $\text{Ru(dcbpyH}_2)_2\text{Cl}_2$ - sensitized TiO_2 fibers are shown in Figure 7. From the absorbance data, the initial rates of the reactions were determined to be first order based on the plot in Figure 8. Given that the ratio of TiO_2 to PAP is 100:1, but not all the TiO_2 is on the surface, and the dye loading on the surface, the reaction is not pseudo-first order. From the plot, the rate constant for the photodegradation of PAP using bare TiO_2 fibers and $\text{Ru(dcbpyH}_2)_2\text{Cl}_2$ - sensitized TiO_2 fibers were determined to be $0.032 \pm 0.003 \text{ min}^{-1}$ and $0.012 \pm 0.002 \text{ min}^{-1}$, respectively while the controls showed no degradation.

Figure 7. Absorption of PAP over time when exposed to no catalyst, $\text{Ru(dcbpyH}_2)_2\text{Cl}_2$ TiO_2 fibers and $\text{Ru(dcbpyH}_2)_2\text{Cl}_2$ - sensitized TiO_2 fibers in dark and under UV irradiation.

Figure 8: First order rate law plot for the degradation of PAP with TiO₂ fibers and Ru(dcbpyH₂)₂Cl₂ - sensitized TiO₂ fibers under UV/visible irradiation.

An equivalent experiment was carried out in a glass beaker which was chosen to filter light at energies higher than 320 nm, therefore blocking any UV irradiation from being absorbed by the catalyst. Again the concentration during the reaction was monitored using UV Vis as shown in Figure 9. Like previously, no degradation was observed for the controls. From the absorbance data, the initial rates were again determined to be first order rate law, this time having $0.014 \pm 0.001 \text{ min}^{-1}$ and $0.012 \pm 0.0002 \text{ min}^{-1}$ for TiO₂ fibers and Ru(dcbpyH₂)₂Cl₂ - sensitized TiO₂ fibers respectively as shown in Figure 10.

Figure 9: Absorption of PAP over time when exposed to no catalyst, $\text{Ru}(\text{dcbpyH}_2)_2\text{Cl}_2$, TiO_2 fibers and $\text{Ru}(\text{dcbpyH}_2)_2\text{Cl}_2$ - sensitized TiO_2 fibers in dark and under visible irradiation.

Figure 10. First order rate law plot for the degradation of PAP with TiO_2 fibers and $\text{Ru}(\text{dcbpyH}_2)_2\text{Cl}_2$ - sensitized TiO_2 fibers under visible irradiation.

The results in Table 1 show that PAP is stable in an aqueous solution both with and without the dye present when irradiated with either UV or visible light. The most efficient catalyst was found to be the bare TiO_2 fibers under UV irradiation. A decrease in the rate of degradation was observed when going from UV to visible irradiation with non-sensitized TiO_2 . The band gap of TiO_2 is in the UV region meaning it will absorb light and create the most

electron-hole pairs in the UV range. The initial rate for the TiO₂ fibers when exposed to visible light were similar to the Ru(dcbpyH₂)₂Cl₂– sensitized TiO₂ fibers when exposed to both UV and visible irradiation. All the fibers with similar rates were all lower in rate than the bare fibers under UV irradiation. The decrease in the initial rate going from the bare fibers under UV irradiation to the dye sensitized fibers under UV irradiation suggests there is a charge transfer from the dye, resulting in a decrease in efficiency.

Table 1. Initial rate constants of PAP degradation using TiO₂ fibers and Ru(dcbpyH₂)₂Cl₂– sensitized TiO₂ fibers in quartz vial and glass beaker.

Photocatalyst	Quartz vial (UV/Visible Irradiation)	Glass beaker (Visible Irradiation)
No Catalyst	No degradation	No degradation
Ru(dcbpyH ₂) ₂ Cl ₂	No degradation	No degradation
TiO ₂ Fibers	$0.032 \pm 3 \times 10^{-3} \text{ min}^{-1}$	$0.013 \pm 5 \times 10^{-3} \text{ min}^{-1}$
Ru(dcbpyH ₂) ₂ Cl ₂ – sensitized TiO ₂ Fibers	$0.012 \pm 2 \times 10^{-3} \text{ min}^{-1}$	$0.012 \pm 2 \times 10^{-3} \text{ min}^{-1}$

The role of the dye was to absorb light in the visible region through a metal to ligand charge transfer (MLCT) transition. This has previously been shown to inject electrons into the TiO₂.^{7, 8, 15} This process would help expand the region of absorption and electron-hole separation following injection as shown in step 1 and 2 of Figure 11. There are competing pathways that decrease efficiency and electron-hole separation under visible irradiation, namely, steps 3 (back electron transfer) and 5 (electron reaction with oxygen). If the rate for the recombination is faster than the rate of radical formation, there will be a decrease in radical formation. This decrease in radical formation will be increased further amplified under UV irradiation because the TiO₂ will be populating the conduction band with electrons from the valence band. A similar mechanism has been shown with the use of 2,4,6-triphenylpyrilium hydrogen sulfate (TPPHS) as a photosensitizer.⁶ It was found using TPPHS as a photosensitizer the rate under UV irradiation increased, while there was a reduction in rate during visible irradiation compared to bare TiO₂. This was attributed to the increase electron hole separation under UV irradiation. Another example uses CdS as a photosensitizer which was able to

increase the rate under visible light, however the material leached Cd^{2+} .⁴ These examples and the current results suggest the photosensitizers do not have a uniform role in the formation of radicals as they do for electron injection in DSSCs. Different photosensitizers have shown different mechanisms suggesting surface modification of TiO_2 with photosensitizers is a more complex system than in a DSSC.^{4-6, 25}

Figure 11: Proposed mechanism for formation of radicals from dye-sensitized TiO_2 fibers.

Ruthenium polypyridyl dyes are known electron injectors, increasing the population of electrons in the conduction band of the TiO_2 .⁷⁻¹² Because there is a decrease in rate of degradation when dye is attached, it supports the preferred pathway for the degradation of PAP progressing through the formation of hydroxyl radicals. Hydroxyl radical formation could be enhanced with hole transport modification such as introduction of poly(ethylene dioxythiophene) (PEDOT) which has been shown to enhance degradation performance.^{26, 27} There are other materials which could also be explored and which are known hole transporting materials such as NiO .²⁸

Conclusion

The results suggest that the electron transfer from the conduction band of TiO_2 does not play a major role in the degradation of PAP. This is based on the decrease in rate of degradation from TiO_2 fibers to dye sensitized TiO_2 fibers under UV irradiation and the consistent rate for the dye sensitized TiO_2 fibers. It is possible that the degradation efficiency would be improved with

the use of a hole-transport dye which would increase the radicals formed from the valence band of TiO₂.

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