

Article Harnessing Evanescent Waves in UV-Irradiated TiO₂-Coated Quartz Optical Fibers Improves Pollutant Degradation in Water

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Abstract: Coupling TiO₂-coated quartz optical fibers (TiO₂-QOFs) with LEDs shows potential in degrading organics in water. Conventional TiO₂-QOFs with thick and compact coatings are inefficient to degrade organic pollutants due to refraction losses. The research focuses on manipulating coating strategies to increase the generation of evanescent waves, which react more efficiently with the coated TiO₂, which shows a crystal structure at anatase/rutile of 85/15. Through the use of dip-coating methods, TiO₂ can be effectively deposited on quartz optical fibers, leveraging the principle of electrostatic attraction. By decreasing TiO₂ dip-coating concentrations from 200 to 10 mg/L, dip-coating duration from 2 to 0.5 h, and coating cycles from 3 to 1, TiO₂ patchiness on quartz fibers was reduced by 50–60%, enhancing the formation of more interspaces between the fiber surfaces and the coatings, which in turn allowed over 90% of evanescent waves in the TiO₂-QOFs. The evanescent wave-dominated TiO₂-QOFs irradiated by 275 nm UV-LED exhibited methylene blue degradation rate constants at around 0.03 h⁻¹ and quantum yields greater than unity, indicating a highly efficient interaction between the evanescent wave and the surface coatings. These findings offer significant insights into optimizing the utilization of evanescent waves in TiO₂-QOFs for pollutant degradation by regulating the coating structures.

Keywords: TiO₂ nanoparticle; evanescent wave; optical fiber; pollutant remediation

1. Introduction

Water pollution caused by organic pollutants is a growing concern worldwide, posing a significant threat to human health and the environment [1-3]. To ensure the long-term sustainability of water resources, it is crucial to develop effective water treatment technologies. Advanced oxidation processes (AOPs) emerged as promising strategies for degrading organic pollutants, including dyes, pharmaceuticals, and endocrine-disrupting compounds [4-6]. AOPs employ highly reactive species to oxidize pollutants into less harmful or non-toxic compounds due to their high efficiency and non-selectivity to degrade a wide range of pollutants and minimal generation of harmful byproducts [7–9]. Among various AOPs, photocatalytic processes using TiO₂ have attracted considerable attention because this process requires little chemical dosage and a lower cost, and TiO₂, as a reactive, nontoxic, inexpensive, and chemically stable photocatalyst, can be used repeatedly [10–12]. Upon UV irradiation, TiO₂ generates electron-hole ($e^{-}h^{+}$) pairs, which participate in redox reactions near/on the TiO₂ surfaces, leading to the formation of highly reactive species [13–15]. However, current photocatalytic reactors, including slurry and fixed-bed reactors, present challenges that limit their practical application. Light scattering and occlusion occur as incident light interacts with suspended TiO_2 particles or the fixed



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). beds and other aqueous constituents, causing the light to disperse in multiple directions. This stops light from penetrating deeper into the reactor and significantly diminishes the energy efficiency of the system [16,17].

TiO₂-coated quartz optical fiber (TiO₂-QOF) technology is a promising solution to overcome the challenges of those conventional reactors associated with light scattering and occlusion [18–23]. When light is delivered into and propagates along TiO₂-QOFs, it is refracted from the low refractive index (RI) optical fiber core into the high refractive index TiO₂ coatings. The direct activation of TiO₂ on the optical fiber surface results in significantly enhanced energy efficiency, providing at least three times higher quantum yields for degrading methylene blue, malic acid, and 4-chlorophenol in water [23–25]. Although TiO₂-QOFs demonstrate considerable potential for effective light utilization, a substantial portion of optical energy is still lost since refracted light will pass through the coated layers and escape from the fiber [26–29]. Therefore, there is a pressing need to enhance the light utilization efficiency of TiO₂-QOFs in order to minimize these energy losses and optimize the performance of photocatalytic systems.

Our latest research unveils a groundbreaking mechanism that facilitates more efficient light interaction with the coated TiO_2 and minimizes energy losses [30,31]. This is achieved by utilizing evanescent waves, which are generated during the total internal reflection (TIR) of light by constructing a porous coating layer instead of a compact TiO_2 layer on the fiber surfaces. By doing so, the external bulk medium around TiO_2 -QOFs with lower RI than the fiber core can fill these interspaces between the fiber and the coated TiO_2 within the porous layer, which consequently enables TIR of light delivered to the fiber and thus generates evanescent waves on the fiber surfaces [32–34]. Evanescent waves are an ideal energy form to activate the coated TiO_2 as they are localized standing waves instead of propagating away from optical fibers as traveling refracted light, and if not absorbed, they will return to the fiber core and be reutilized further along the fiber [33,34]. With such remarkable properties, evanescent waves demonstrate quantum yields that exceed those of refracted light by more than two-fold [30]. Maximizing evanescent waves is a coveted goal for minimizing energy losses in TiO_2 -QOFs but remains elusive and needs further exploration.

A critical aspect of evanescent wave control is the ability to tailor the coating structure on the fiber surfaces, as it directly influences evanescent wave propagation and interaction with the surrounding media. To promote the generation of evanescent waves, more interspaces between the fiber surfaces and the coated TiO₂ need to be created, which allows lower RI water to fill to facilitate TIR. One of the coating structures to quantify such interspaces is patchiness (*p*), which defines the ratio of the area where TiO₂ is directly attached to the fiber surface to the total fiber surfaces [30]. Additionally, the interspace distance (*z*) regulates the quantity of evanescent wave energy absorbed and returned. Specifically, the evanescent wave energy that penetrates over a distance of *z* is absorbed, while the energy that does not cross *z* and reach the TiO₂ coating is returned to the fiber [31]. For a long TiO₂-QOF length, the *z* of coatings varies but could be normalized to an average value, denoted as z_a , to quantify the overall evanescent wave absorption. Therefore, it is imperative to establish a comprehensive understanding of the relationship between coating structures (*p* and z_a) and evanescent wave generation to unlock the full potential of TiO₂-QOFs for efficient pollutant degradation in water.

In this study, TiO₂-QOFs were fabricated using a dip-coating method, which was chosen for its simplicity, cost-effectiveness, and ease of control, making it well-suited for large-scale production [25,30,31]. The mechanism of TiO₂ deposition on quartz optical fiber was explored and subsequently leveraged to regulate the p and z_a of coatings by varying coating conditions, including the concentration of the dipped solution, dipping duration, and dip-coating cycles. To determine the optimal coating structure for maximizing evanescent waves, the resulting p and z_a were further correlated with the generation of the two energy forms (i.e., evanescent waves and refracted light) using the energy balance model developed in a previous study [30]. Finally, the performance of the evanescent wave-driven TiO₂-QOFs was evaluated by examining their ability with a common dye, methylene

blue (MB). These studies provided valuable insights into the practical applications of the TiO_2 -QOFs and demonstrated their potential for use in environmental remediation.

2. Materials and Methods

2.1. Chemicals and Experimental Materials

Reagent-grade chemicals, including MB and TiO₂ (P25, anatase/rutile 85/15, particle size 21 nm), were purchased from Sigma-Aldrich without further purification. Their stock solutions were prepared using double deionized (DDI) water (18.2 M Ω -cm) prepared by a Nanopure system (Barnstead, NH, USA).

Uncoated quartz optical fibers were prepared by cutting the purchased quartz optical fibers (FT1000UMT, Thorlabs, Newton, NJ, USA) into segments of specified lengths using a ruby blade. The segments were soaked in acetone for 24 h, then 1 M KOH for another 24 h to remove their cladding, and finally washed with DDI water [25]. Both ends of the uncoated fiber segments were polished using a polishing assembly (D50SMA, Thorlabs) with LF30P, LF5P, and LF03P fiber polishing paper in that order. The clarity of both ends was critically examined using a fiber inspection scope (FS201, Thorlabs) to ensure a good light transmission.

2.2. Modeling the Light Propagation in TiO₂-QOFs as a Function of Coating Structures

The energy balance model previously developed was employed to study the evanescent waves and refracted light in the coated optical fibers as functions of coating structures [30]. The model could simulate the light rays at different angles emitted from an LED light source and launching into the TiO₂-QOFs. Each light ray continuously struck the inner fiber surfaces and generated evanescent waves at the interface, which was covered with water, and then activated TiO₂ or generated refract light at the interface, which was attached with TiO₂. The radiant flux dissipation of evanescent waves ($E_{E,dis}$) and that of refracted light ($E_{R,dis}$) were calculated with Equations (1) and (2), respectively. Their sum was equal to the overall radiant flux dissipation (E_{dis}) as shown in Equation (3).

$$E_{E,dis} = E_i \sum_{\theta=\theta_m}^{90^{\circ}} \frac{(1-p) \cdot e^{-\frac{z_a}{\Lambda}} \cdot \left\{ 1 - \left[(1-p) \cdot (1-e^{-\frac{z_a}{\Lambda}}) + p \cdot (1-T) \right]^{\left\lfloor \frac{L}{D \cdot t_{an\theta}} \right\rfloor} \right\}}{(1-p) \cdot e^{-\frac{z_a}{\Lambda}} + p \cdot T}$$
(1)

$$E_{R,dis} = E_i \sum_{\theta=\theta_m}^{90^{\circ}} \frac{p \cdot T \cdot \left\{ 1 - \left[(1-p) \cdot (1-e^{-\frac{z_a}{\Lambda}}) + p \cdot (1-T) \right]^{\left\lceil \frac{L}{D \cdot tan\theta} \right\rceil} \right\}}{(1-p) \cdot e^{-\frac{z_a}{\Lambda}} + p \cdot T}$$
(2)

$$E_{dis} = E_{E,dis} + E_{R,dis} = E_i \sum_{\theta=\theta_m}^{90^{\circ}} \left\{ 1 - \left[p \cdot \left(1 - e^{-\frac{z_a}{\Lambda}} \right) + (1-p) \cdot (1-T) \right]^{\left\lceil \frac{L}{D \cdot t_{an\theta}} \right\rceil} \right\}$$
(3)

where E_i was the radiant flux delivered into TiO₂-QOFs; θ was the incident angle of light rays that showed a range from a minimal θ (θ_m) to 90°; L was the fiber length and D was the fiber diameter; Λ was the penetration depth of evanescent waves from the fiber surface to the external medium of the fiber, which was calculated using Equation (4); and T was the transmittance of refract light from the fiber core to the coating as calculated by Equation (5).

$$\Lambda = \frac{\lambda}{4\pi} \cdot \left(n_f^2 \cdot \sin^2\theta - n_e^2\right)^{-1/2} \tag{4}$$

$$T = 1 - \frac{1}{2} \left\{ \left[\frac{n_f \cos\theta - n_c \sqrt{1 - \left(\frac{n_f}{n_c} \sin\theta\right)^2}}{n_f \cos\theta + n_c \sqrt{1 - \left(\frac{n_f}{n_c} \sin\theta\right)^2}} \right]^2 + \left[\frac{n_f \sqrt{1 - \left(\frac{n_f}{n_c} \sin\theta\right)^2} - n_c \cos\theta}{n_f \sqrt{1 - \left(\frac{n_f}{n_c} \sin\theta\right)^2} + n_c \cos\theta} \right]^2 \right\}$$
(5)

where λ was the light wavelength, and n_f , n_e , and n_c were the RI of the optical fiber, RI of the external medium of the fiber, and RI of coatings, respectively.

Due to the return of evanescent waves and reflected light from the refraction spot, there was still radiant flux emitting out of the distal fiber end (E_{out}), which was equal to the difference between E_i and E_{dis} . The emitted radiant flux from the distal end contributed by the returned evanescent waves ($E_{E,return}$) and that by the reflected radiant energy from refraction spots ($E_{R,reflect}$) were determined by Equations (6) and (7), respectively.

$$E_{E,return} = (E_i - E_{dis}) \sum_{\theta=\theta_m}^{90^{\circ}} \frac{(1-p) \cdot \left(1 - e^{-\frac{z_a}{\Lambda}}\right)}{p \cdot (1-T) + (1-p) \cdot \left(1 - e^{-\frac{z_a}{\Lambda}}\right)}$$
(6)

$$E_{R,reflect} = (E_i - E_{dis}) \sum_{\theta=\theta_m}^{90^{\circ}} \frac{p \cdot (1-T)}{p \cdot (1-T) + (1-p) \cdot \left(1 - e^{-\frac{z_a}{\Lambda}}\right)}$$
(7)

The generated evanescent wave energy $(E_{E,g})$ was the sum of $E_{E,dis}$ and $E_{E,return}$ while the generated refracted light energy $(E_{R,g})$ is the sum of $E_{R,dis}$ and $E_{R,reflect}$.

2.3. Experimental Setup and Procedures

TiO₂-QOFs were fabricated by immersing the uncoated optical fiber segments with the reactor filled with TiO₂ suspensions at different concentrations for different durations and cycles to produce the coating layers with different *p* and z_a . The images of the coated fiber surfaces were obtained by SEM (JSM-6700F, JEOL, Tokyo, Japan).

The experiment, including irradiance measurement and MB degradation, was carried out in a well-mixed batch reactor depicted in Figure 1. The reactor consisted of a cylindrical glass vessel of 80 mL volume, 8.6 cm in length, and 3.5 cm in inner diameter. It was equipped with a magnetic stirrer (F203A0160, VELP, Usmate, Italy) at the bottom for mixing, a 275 nm LED, and an optical meter (RPS900-R, International Light Technologies, Peabody, MA, USA). A single uncoated optical fiber or fabricated TiO₂-QOF was installed in the reactor, with one end attached to the LED lamp and the other connected to the optical meter.



Figure 1. The photocatalytic reactor.

The installed reactor was then used to experimentally monitor E_{dis} of TiO₂-QOFs, which was the difference between E_i and E_{out} , while E_{out} of the uncoated optical fiber in water could be regarded as E_i because, in this case, RI of the fiber was higher than RI of water leading to TIR within the fiber presenting no energy losses. E_{dis} was thus expressed as Equation (8).

$$E_{dis} = (I_i - I_{out}) \cdot A \tag{8}$$

where I_i was the irradiance measured from the optical meter (W/cm²), and *A* was the cross-sectional area of optical fibers (cm²). The obtained E_{dis} of each TiO₂-QOF in air and that of water were used to determine its coating structure by substituting the values of E_{dis} to Equation (3) to obtain *p* and z_a , which were further input to the model to investigate the relationships between different coating structures and energy forms.

The reactor was also used to conduct MB degradation by the UV-irradiated TiO₂-QOFs under normal conditions and at a pH of 7. MB concentrations were determined by UV/VIS spectrophotometer (Lambda 25, PerkinElmer, Waltham, MA, USA). The degradation rate constants were obtained by plotting MB concentration as a function of time. The quantum yields (η) of MB degradation were calculated using Equation (9).

$$\eta = \frac{k \cdot V \cdot ([MB]_0)^1}{E_{dis}} \tag{9}$$

where $[MB]_0$ was the initial MB concentration at 6.25×10^{-6} mole/L, and V was the liquid volume (L).

3. Results and Discussion

3.1. Coating TiO₂ on Quartz Optical Fibers

The fundamentals of dip-coating TiO₂ on quartz optical fibers were first investigated, which may pave the way for precise regulation of the coating structures to generate evanescent waves. Although characterizing the coating morphology during the dip-coating process is challenging, it can be inferred by monitoring the real-time light dissipation. Figure 2a illustrates the relationship between the percentage of E_{dis} to E_i of TiO₂-QOFs as a function of dip-coating duration with four TiO₂ dip-coating concentrations at 6, 10, 40, and 200 mg/L. An initial rapid increase in E_{dis}/E_i was observed for all concentrations, followed by a slower rate of increase, eventually reaching a plateau. The rate and extent of light dissipation also depend on the TiO₂ concentration. The optical fiber dipping with 200 mg/L TiO₂ showed the most significant improvement in E_{dis}/E_i , reaching 0.3 at the first 0.5 h and slightly increasing to 0.32 after 3 h. In contrast, the fiber dipping with lower TiO₂ concentrations required longer durations to achieve a similar level of light dissipation (i.e., 1 h for 40 mg/LTiO₂ and 3 h for 10 mg/L TiO₂ to reach E_{dis}/E_i of 0.3). The slowest increase in E_{dis}/E_i was observed for 6 mg/L TiO₂, which only reached E_{dis}/E_i of 0.15 after 3 h.



a

Figure 2. Cont.

b

Optical fiber (SiO₂) / ZPC=2~3.5 Media: TiO₂ slurry, pH≈5.7 TiO2 with positive surface charge moves towards negative fiber e ZPC=6.1-6.8 Ŧ Đ Ð \oplus Θ \oplus \oplus \oplus \oplus \oplus Æ e \oplus \oplus Θ \oplus \oplus \oplus $|\tilde{\oplus}|^{\oplus}$ Æ Θ \oplus E \oplus \oplus Tip \square \oplus Ð Negatively charged ion Double laye Stern layer thickness up to 30nm Positively charged ion Double layer UV light thickness up to 30nm С

X50.000 WD 7.5mn 5.0kV

Figure 2. Dip-coating of TiO_2 on quartz optical fibers. (a) The percentage of the radiant flux dissipation to the radiant flux delivered to fibers (E_{dis}/E_i) as a function of dip-coating duration of TiO_2 at different concentrations; (b) the mechanism of TiO_2 loaded on quartz optical fibers through electrostatic attraction; (c) Scanning electron microscope image of TiO₂-QOF surfaces. (Conditions: light wavelength = 275 nm, light intensity = 0.73 mW/cm^2 , optical fiber diameter = 1 mm).

Electrostatic attraction is proposed to be the primary mechanism for TiO₂ particles loaded on the quartz optical fibers as shown in Figure 2b. Quartz is composed of mainly silicon dioxide (SiO₂) and has a high density of surface hydroxyl (OH) groups that can undergo ionization and acquire a net charge when in contact with water [35–37]. At a pH below its point of zero charge (PZC) at around 2–3.5, the surface of SiO_2 is mostly covered with positively charged $SiOH_2^+$ groups due to protonation. As the pH increases beyond this point, deprotonation occurs, where a proton is lost, forming neutral SiOH groups. Further increasing pH leads to a larger number of SiO⁻ groups. Similarly, TiO₂ in suspension also carries a surface charge depending on its PZC, which is around 6.1–6.8. During the dip-coating process, the pH of the TiO_2 suspension was around 5.7, which

resulted in TiO₂ particles carrying net positive charges and the quartz fibers carrying net negative charges. We propose that electrostatic attraction promotes the adhesion of TiO₂ particles onto the quartz fiber surface. On the other hand, there is an electric double layer that includes two parallel layers of charge appearing on both the surfaces of quartz and TiO₂, hindering the adhesion of TiO₂ particles [38]. We propose that the eventually formed porous and patchy TiO₂ coating layers, as shown in the SEM images (Figure 2c), is the result of this repulsion effect. With higher concentrations of TiO₂ suspension, the double layer thickness was very likely to be pressed to weaken the repulsion, which enhances the adhesion of TiO₂ particles and leads to more TiO₂ loaded on the quartz surfaces.

Therefore, the rapid light dissipation at the beginning may be attributed to the rapid deposition of TiO_2 particles on the fiber surface through the balance between the electrostatic attraction and the repulsion of the double layer, hindering the adhesion of TiO_2 particles. As the coating builds up, the rate of light dissipation increase slows down and stabilizes until it approaches a saturation point of TiO_2 deposition. TiO_2 concentration and dipping durations in the dip-coating thus play a crucial role in modulating the TiO_2 deposition as well as light dissipation. In addition, implementing additional coating cycles could serve as a viable strategy to increase the TiO_2 deposition if needed. By carefully implementing these strategies, it is feasible to fabricate coatings tailored to achieve the desired light dissipation.

3.2. Effects of Dip-Coating Conditions on Coating Structures and the Resulting Evanescent Waves

To control the amount of TiO₂ particles deposited on the quartz optical fiber and thus the coating structures, the dip-coating concentrations were varied. To investigate the effect of TiO₂ dip-coating concentration, 1 h of dipping duration was selected. Figure 3a shows the radiant flux dissipation in TiO₂-QOFs when surrounded by air ($E_{dis,air}$) and when immersed in water ($E_{dis,water}$), which resulted from dipping the optical fiber in TiO₂ suspensions at concentrations of 10, 40, and 200 mg/L. With an increasing TiO_2 dip-coating concentration, $E_{dis,air}$ increased by 1.5 times while $E_{dis,water}$ increased by 1.6 times. The enhanced $E_{dis,air}$ and $E_{dis,avater}$ were because the increased TiO₂ concentrations enabled more TiO₂ particles deposited on the optical fiber, which leads to more light being absorbed by the surface coated TiO_2 . On the other hand, dipping optical fiber in all three TiO_2 suspensions at concentrations of 10, 40, and 200 mg/L resulted in higher $E_{dis, water}$ than $E_{dis,air}$, with enhancement factors of approximately 1.6 to 1.9 times. The higher $E_{dis,auter}$ indicated the presence of evanescent waves in the fabricated TiO₂-QOFs [30,31] because when the fiber was immersed in water compared with in air, the difference between n_f and n_e became smaller, which gives higher values of Λ and consequently allows evanescent waves to penetrate further to activate more TiO_2 .

We then employed the energy balance model to examine the impacts of the coating structures resulting from various dip-coating concentrations on the behavior of evanescent waves. To obtain coating structures fabricated with different TiO₂ concentrations, the obtained $E_{dis,air}$ and $E_{dis,vater}$ in Figure 3a were substituted to Equation (3) to calculate p and z_a . The results shown in Figure 3b indicate that p increased by 1.5 times from 0.005 to 0.013 while z_a decreased by 31% from 214 to 147 nm, which resulted from increasing TiO₂ concentrations from 10 to 200 mg/L. Based on the p and z_a obtained above, $E_{E,dis}$ and $E_{R,dis}$ were calculated using Equations (1) and (2) while $E_{E,return}$ and $E_{R,reflect}$ were calculated using Equations (6) and (7), which were then compared as shown in Figure 3c. Dipping optical fibers to all three TiO₂ suspensions resulted in evanescent wave-dominated systems, as the percentages of the evanescent wave generation (i.e., $E_{E,g}$, which is equal to the sum of $E_{E,dis}$ and $E_{E,return}$) to E_i accounted for over 90%. Reducing the TiO₂ concentrations from 200 to 10 mg/L even allowed 5% more $E_{E,g}$ and reduced the refracted light generation (i.e., $E_{R,g}$, which is equal to the sum of $E_{R,dis}$ and $E_{R,reflect}$) by 46%. These findings suggest the TiO₂ coating layer fabricated with such ranges of TiO_2 concentrations allows for the creation of a low p for facilitating the generation of evanescent waves that dominate the energy form in TiO₂-QOFs. Apart from this, $E_{E,return}$ increased by 40% and $E_{E,dis}$ decreased by 66%

with reducing TiO₂ concentrations, which were attributed to the increased z_a , reducing the evanescent waves being absorbed and returning more evanescent waves to the fiber. Such results of regulating coating structures to modulate evanescent waves allow the neglectable refraction loss and a saving of 62% optical energy in the TiO₂-QOFs. The saved energy can be further utilized with the extended optical fiber length and thus potentially enhance the photocatalytic performance.



Figure 3. Cont.



Figure 3. Effects of TiO₂ dip-coating concentrations on (**a**) the radiant flux dissipation of TiO₂-QOF in air and that in water; (**b**) TiO₂ coating structures (p and z_a); (**c**) the dissipated evanescent waves ($E_{E,dis}$) and refracted light ($E_{R,dis}$) as well as the returned evanescent waves ($E_{E,return}$) and the reflected light from refraction spots ($E_{R,reflect}$) obtained from energy balance model. (Conditions: light wavelength = 275 nm, light intensity = 0.73 mW/cm², optical fiber diameter = 1 mm).

Regulating the dipping duration also leads to similar trends to the above findings, as it also exerts control over light dissipation, as evidenced in Figure 2a. By keeping the TiO_2 dip-coating concentration steady at 40 mg/L but extending the dipping duration from 1 to 2 h, the light dissipation becomes the same as that of a coating produced from TiO_2 at 200 mg/L with a duration of 1 h, thus resulting in similar coating structures. This is attributed to the weaker electrostatic attraction resulting from a lower dip-coating concentration, which slows down TiO_2 deposition and hence requires a longer time to deposit an equivalent amount and coating structure of TiO_2 . On the other hand, reducing the dipping duration to approximately 15 min results in light dissipation equivalent to a coating formed with TiO_2 at 10 mg/L over 1 h, as the stronger electrostatic attraction needs a shorter dipping duration.

The coating cycle is another critical parameter to regulate the coating structure in addition to TiO₂ concentrations and dipping duration. Its effects were investigated similarly to the above studies except for maintaining a TiO₂ suspension concentration of 40 mg/L and dipping duration of 1 h. With increasing coating cycles from 1 to 3, $E_{dis,air}$ and $E_{dis,avater}$ also increased due to additional TiO₂ coating layers deposited on the optical fiber (Figure 4a). There were also increases from $E_{dis,air}$ to $E_{dis,avater}$ for one or multiple coatings, which were caused from the involvement of evanescent waves. Figure 4b shows that *p* doubled while z_a decreased by 30% with an increase in coating cycles from 1 to 3. The increased *p* resulted in 40% increases in refracted light and 3% less evanescent waves, which, however, still dominated in the TiO₂-QOFs (Figure 4c). The reduced z_a allowed more evanescent waves to reach TiO₂ layers and gave a higher overall light dissipation. The aforementioned results demonstrate the advantage of dip-coating for modulation of evanescent waves. Dip-coating is simple and cost-effective because it only requires TiO₂ suspension to produce uniform coating layers. This practicality makes it suitable for practical applications, compared with chemical vapor deposition which demands high temperatures and specialized equipment

and spray-coating or spin-coating, which struggles to provide uniform coating layers on round surfaces of optical fibers [39]. Additionally, dip-coating affords us the ability to easily manage coating conditions and maintain a steady generation of evanescent waves. Nevertheless, the disadvantages of dip-coating include the difficulty of controlling the photocatalyst crystalline phase and needing hours for coating.



Figure 4. Cont.



Figure 4. Effects of dip-coating cycles on (**a**) the radiant flux dissipation of TiO₂-QOF in air and that in water; (**b**) TiO₂ coating structures (*p* and *z_a*); (**c**) the dissipated evanescent waves ($E_{E,dis}$) and refracted light ($E_{R,dis}$) as well as the returned evanescent waves ($E_{E,return}$) and the reflected light from refraction spots ($E_{R,reflect}$) obtained from energy balance model. (Conditions: light wavelength = 275 nm, light intensity = 0.73 mW/cm², optical fiber diameter = 1 mm).

3.3. Enhanced Pollutant Degradation Performance

After establishing the methods to fabricate TiO₂-QOFs with high percentages of evanescent wave generation, we then investigated the impacts of the enhanced quantity of evanescent waves in TiO₂-QOFs on their photocatalytic performance, which is described by their ability to generate reactive species to degrade a common dye, MB. Figure 5 presents the MB degradation by the 275 nm UV-LED irradiated uncoated optical fibers and TiO_2 -QOFs. The uncoated optical fiber (i.e., zero patchiness) exhibited a degradation rate constant (k) of 0.004 h^{-1} , which was attributed to the direct MB photolysis by the evanescent waves dissipated from the fiber surfaces owing to the lower RI of MB solution than the quartz fiber leading to TIR. The highest quantum yield (η) of around 1.09 was observed for the MB degradation by evanescent waves. The high quantum yield of the process greater than unity demonstrated the high energy efficiency of evanescent waves interacting with the surrounding media of the fiber. On the other hand, coating TiO_2 on optical fibers at p of 0.009 and z_a of 172 nm significantly enhanced the MB degradation rate constant to 0.029 h⁻¹, which is 6.7 times higher than that of the direct MB photolysis. The unchanged η of 1.07 suggests that the MB degradation via the TiO_2 activation was also achieved by evanescent waves. Despite the increased absorption of evanescent waves by TiO₂, these reactions enhanced MB degradation rates without wasting optical energy, thus maintaining the quantum yields unaltered. The enhanced MB degradation rate constants and unchanged quantum yields of MB degradation indicate the enhanced ability to generate reactive species and concurrently translates to heightened photocurrent responses in TiO₂-QOFs, leading to a marked enhancement in photocatalytic performance. However, with the increases in p and decreases in z_a , although more light energy participated to enhance the production of reactive species, which sightly increases k by 15%, refraction losses increased, which resulted in a significant decrease of η by 38%.



Figure 5. (a) MB degradation by the 275 nm UV-LED irradiated uncoated optical fibers and TiO₂-QOFs. (Conditions: $[MB]_0 = 6.25 \times 10^{-6} \text{ mole/L}$, pH = 7, V = 80 mL, light wavelength = 275 nm, light intensity = 0.73 mW/cm², optical fiber diameter = 1 mm); (b) MB degradation mechanism by TiO₂ irradiated by 275 nm evanescent waves from quartz optical fibers.

The mechanism of MB degradation by the UV-irradiated TiO₂-QOFs is also proposed as shown in Figure 5b. When TiO₂ receives the evanescent waves dissipated from quartz optical fibers whose photon energy is 4.5 eV and higher than the bandgap of TiO₂ at around 3.2 eV, the e⁻ is excited from the valence band to the conduction band of TiO₂ and leaves behind a positively charged h⁺ in the valence band. The excited e⁻ and h⁺ then react with water and oxygen molecules adsorbed on the surface of the TiO₂. The h⁺ oxidizes water or hydroxide ions to generate hydroxyl radicals (HO•), which are highly reactive. On the other side, the e⁻ reduces oxygen to produce superoxide ions (O₂•⁻), which can further generate other reactive oxygen species (ROS), such as H₂O₂ and HO•. These generated ROS, particularly HO•, oxidize MB molecules, resulting in the breakage of chemical bonds to form smaller, less colored, and more biodegradable or mineralizable compounds. Ideally, the photocatalytic process continues until MB and its intermediate degradation products are completely mineralized into harmless substances, such as water, carbon dioxide, and simple inorganic ions [25].

These findings underscore the significant influence of evanescent waves, specifically their role in enhancing the photocatalytic degradation efficiency of TiO_2 -QOFs. Firstly, evanescent waves are standing waves that exist on the surfaces of optical fibers, and if not absorbed, they return to the fiber core rather than escaping away from the fiber surfaces. This characteristic reduces the wasted light caused by refraction and results in high energy efficiency. Secondly, the returning nature of evanescent waves means that light can be transmitted over greater distances, allowing for an extension of the fiber length. The increase in fiber length, in turn, enhances surface reactive sites and thus improves the degradation rate of pollutants. Finally, the generation of evanescent waves is facilitated by a porous coating layer; with a lower patchiness of the coatings, fewer photocatalysts are loaded, which reduces the chemical cost. Therefore, manipulating evanescent waves in TiO_2 -QOFs brings forth higher energy efficiency, higher removal efficiency, and costeffectiveness in photocatalytic pollutant degradation.

The application of TiO₂-QOFs for dye removal has been evaluated considering recently reported data demonstrating the degradation rate constants of various dyes, including MB, Methyl Orange (MO), Reactive Red 195 (RR195), Reactive Red 35 (RR35), and Rhodamine B (RB) by different TiO₂ composites [40–44]. These tests were conducted in a suspension system under solar light and UV light, revealing degradation rate constants between 0.005 and 0.087 min^{-1} as shown in Table 1. These results suggest a promising feasibility of TiO_2 -QOFs if coating these TiO_2 composites on optical fibers in dye removal applications, exhibiting high energy efficiency. Furthermore, considering the photocatalytic performance of TiO₂-QOFs under both solar and UV light, it is highly plausible that these materials could offer a sustainable and efficient solution for dye degradation in various environmental settings. These findings developed from this study are not limited to TiO₂-QOFs alone. We propose other photocatalysts, such as ZnO and Fe_2O_3 , could also be coated on quartz optical fibers by the same electrostatic attraction mechanism because the pH of ZPC for ZnO is around 7 while the value for Fe_2O_3 is around 8 [45,46], which allow them to be positively charged during dip-coating and thus attracted by the quartz fiber surfaces with negative charges. This broader applicability of the findings underscores the potential of our approach to remove various dyes using different photocatalyst-coated optical fibers.

Table 1. Comparison of degradation rate constants of different dyes by TiO₂ composites.

Dye	TiO ₂ Composites	Radiation	Degradation Rate Constants (min ⁻¹)	Ref.
Methylene blue (MB)	2.5 wt% MoS ₂ /TiO ₂ at 0.5 g/L	350–1100 nm at 300 W	0.005	[40]
Methyl Orange (MO)	Ag/TiO ₂ at 2 g/L	UVA at 11 W	0.011	[41]
Reactive Red 195 (RR195)	Ag/ Fe_3O_4 /Ti O_2 at 0.1 g/L	UVA at 27 W	0.077	[42]
Reactive Red 35 (RR35)	20 wt% Activated carbon/TiO ₂ at 0.1 g/L	Solar light	0.087	[43]
Methylene blue (MB)	Chitosan/TiO ₂	365 nm at 64 W	0.081	[44]
Rhodamine B (RB)	Chitosan/TiO ₂	365 nm at 64 W	0.058	[44]

4. Conclusions

This study investigates coating strategies for constructing TiO_2 coating layers on quartz optical fibers with the aim of enhancing the generation of evanescent waves. Expanding upon that foundation developed in our former work [30], which revealed the energyefficient interaction between evanescent waves and the surface coated TiO_2 on optical fibers, different conditions of dip-coating were examined in this work with a purpose of exploring the ability of manipulating evanescent waves generated in TiO_2 -QOFs. By decreasing the TiO₂ dip-coating concentrations, reducing the duration of dip-coating, and coating fewer cycles, the TiO₂ coating layers with a *p* less than 0.018 and z_a higher than 122 nm can be created on quartz optical fibers. These coating structures subsequently allow over 90% of the light delivered to the fiber to dissipate as evanescent waves. Moreover, this study further explored the ability of evanescent waves in enhancing pollutant degradation by correlating the harnessed evanescent waves and quantum yields of MB degradation. With increasing evanescent waves generated in TiO₂-QOFs, the quantum yields increased due to the efficient interaction of evanescent waves with the coated TiO₂, reducing wasted light. When evanescent waves were counted for over 95% of the light delivered to the fiber, the quantum yields were even greater than unity. The findings obtained from this study provide significant insights into the utilization and optimization of evanescent waves in TiO₂-QOFs for pollutant degradation. These findings have substantial implications for the development of advanced photocatalytic systems and offer great potential for more effective and environmentally friendly solutions in pollution control and remediation.

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