Research Article

Photocatalytic Bactericidal Efficiency of Ag Doped $\text{TiO}_2/\text{Fe}_3\text{O}_4$ on Fish Pathogens under Visible Light

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This research evaluates photocatalytic bactericidal efficiencies of Ag- $\text{TiO}_2/\text{Fe}_3\text{O}_4$ in visible light using target pollutants that include *Aeromonas hydrophila*, *Edwardsiella tarda*, and *Photobacterium damsela* subsp. *piscicida*. The investigation started with Ag- $\text{TiO}_2/\text{Fe}_3\text{O}_4$ synthesis and calcination followed by a series of product tests that include the examination of crystallite phase, light absorption, element composition morphology, and magnetic properties. The results of the experiment indicate that Ag and Fe_3O_4 significantly enhanced the light absorption capacity of TiO_2 in the entire visible light range. The Ag- $\text{TiO}_2/\text{Fe}_3\text{O}_4$ prepared in this study displays significantly enhanced visible light absorption and narrowed band gap energy. The magnetic property of Ag- $\text{TiO}_2/\text{Fe}_3\text{O}_4$ made it easy for retrieval using a permanent magnet bar. The photocatalytic activity of Ag- $\text{TiO}_2/\text{Fe}_3\text{O}_4$ remains above 85% after three application cycles, which indicates high and favorable efficiency in bactericidal evaluation. The experiments have proved that the Ag- $\text{TiO}_2/\text{Fe}_3\text{O}_4$ magnetic photocatalyst is a promising photocatalyst for antibacterial application under visible light.

1. Introduction

Bacterial pathogens are a main cause of fish mortalities in cultured fish and occasionally in wild fish. As facultative pathogen exists for both fish and human [1, 2], human infections caused by pathogens transmitted from fish or aquatic environment are quite general. Such infection varies by seasons, dietary habits, and the immune system status of the exposed individual. Traditional methods such as chlorination are chemical intensive and have many disadvantages. For example, chlorine used in water treatment for disinfection can react with organic material to generate carcinogenic chloroorganic compounds. Moreover, certain pathogens, bacteria, and protozoans have been known to be resistant to chlorine disinfection [3].

Applications of photocatalytic processes are viable solutions to environmental problems. Heterogeneous photocatalytic oxidation (PCO) has been proposed as one of the advanced oxidation techniques for mineralization of hydrocarbon pollutants. PCO helps to create strong oxidation agents that breakdown organics to CO_2 in the presence of the photocatalyst, H_2O , and light. Heterogeneous systems also have the advantages of minimal waste generation and reusability of catalysts.

TiO_2 , one of the most promising semiconductor photocatalysts for removing pollutant and cleaning water, is of low cost, nontoxic, and physically and chemically stable. TiO_2 particles are both photocatalytic and antimicrobial [4]. Anatase TiO_2 is superior to rutile and brookite for organic compound removal. However, its wide band gap (3.2 eV)

allows it to be activated only by UV. Also, the high rate of electron-hole (e^- - h^+) recombination in TiO_2 particles results in low photocatalytic efficiency. Doping TiO_2 with various transition metal ions narrows the band gap [5] and expands the photoresponse of TiO_2 into visible spectrum [6]. Also, electron transfer between those metal ions and TiO_2 can alter e^- - h^+ recombination as the metal ions are incorporated into the TiO_2 lattice. Feng et al. [7] have studied the antibacterial mechanism of Ag^+ on bacteria and found that Ag^+ deprives DNA molecules' replication abilities. In addition, Ag^+ increases visible light absorption and holds up the e^- - h^+ recombination of TiO_2 .

Many of the particles used in the separation technology are superparamagnetic, which can be magnetized with an external magnetic field and redispersed upon the removal of magnet [8, 9]. For example, the magnetic property Fe_3O_4 helps to enhance the recovery of the catalyst via external magnetic field. Magnetic Fe_3O_4 particles suspended in carrier fluids are referred to as magnetic fluids. Additionally, Fe_3O_4 also enhances the visible light absorption which resulted from the band gap reduction [10].

2. Materials and Methods

2.1. Materials. The chemicals used in this study include titanium (IV) isopropoxide (98% Acros Organics), isopropyl alcohol (99.9% Carlo Erba), acetylacetone (99.5% Carlo Erba), silver nitrate (99.8% Sigma-Aldrich), ferric chloride anhydrous (98% Katayama Chemical Inc.), ferrous chloride (97% Katayama Chemical Inc.), and sodium hydroxide (97% Katayama Chemical Inc.). These chemicals are analytical reagent grades and used without further modification.

2.2. Synthesis of $\text{Ag-TiO}_2/\text{Fe}_3\text{O}_4$. The $\text{Ag-TiO}_2/\text{Fe}_3\text{O}_4$ magnetic photocatalyst was synthesized in two steps. First, magnetite (Fe_3O_4) nanoparticles were synthesized via coprecipitation method, in which FeCl_3 anhydrous and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ salts in the molar ratio of 2:1 were dissolved and vigorously stirred in double-distilled water. NaOH was then dropped slowly into the solution until a large amount of black precipitates formed. The resulting precipitates were collected using a magnet and washed several times with double-distilled water and ethanol. The reaction in this process is as follows:

In the second step, $\text{Ag-TiO}_2/\text{Fe}_3\text{O}_4$ composite particles were prepared using modified sol-gel method. Acetylacetone (Acac), as a chelating agent, was added into isopropyl alcohol and stirred magnetically. Titanium isopropoxide (TTIP) was then added gradually to the mixture with Acac:IPA:TTIP in molar ratio of 2.84:23.64:1. An appropriate volume of aqueous silver nitrate was added to the titanium solution to attain 1 wt% of Ag on TiO_2 and stirred vigorously for 30 minutes. Meanwhile, Fe_3O_4 particles were dispersed in isopropyl alcohol and sonicated in an ultrasonic apparatus for 10 minutes. Thereafter, slowly add the mixture of Ag-TiO_2 into Fe_3O_4 suspension with TTIP: Fe_3O_4 ratio of 10 (weight basis) and stir the mixture at room temperature for 3 hours

to ensure uniform composition. The obtained suspension was placed in a hot air oven at 90°C for the particles to dry. Finally, the composite particles were calcinated in oxygen at 450°C for 3 hours to form $\text{Ag-TiO}_2/\text{Fe}_3\text{O}_4$.

2.3. Characterization of $\text{Ag-TiO}_2/\text{Fe}_3\text{O}_4$. The properties of $\text{Ag-TiO}_2/\text{Fe}_3\text{O}_4$ magnetic photocatalyst were characterized with various instruments. The crystal structure of the particles was characterized with X-ray diffraction (XRD) on a Bruker AXS diffractometer with $\text{CuK}\alpha$ radiation. The X-ray was generated with a current of 40 mA and a potential of 40 kV in angular range (2θ) from 10° to 80° . The UV-Visible diffuse reflectance spectra in the range of 320–800 nm were acquired from a Hitachi U3501UV-visible diffuse reflectance spectrophotometer (UV-Vis DRS) equipped with integrating sphere. Pure BaSO_4 powder was used as a reflectance standard. Transmission electron microscopy (TEM) observation of the samples was performed on a HITACHI 7500 transmission electron microscope operated at 80 kV. The magnetization of photocatalyst was measured using superconducting quantum interference device (SQUID).

2.4. Evaluation of Photocatalytic Bactericidal Activities. The research team has evaluated photocatalytic bactericidal activities using modified antibacterial drop test. In order to differentiate the effect of TiO_2 and silver, the experiment was conducted both under visible light and in dark to block photocatalytic process to assure that the bactericidal activity is exclusively from silver. Fish pathogens used in the experiment included *Aeromonas hydrophila* (BCRC13018), *Edwardsiella tarda* (BCRC10670), and *Photobacterium damsela* subsp. *piscicida* (BCRC17065). Bacterial cells were collected via centrifugation at 9500 rpm for 10 minutes to remove supernatants. The pellets were then rinsed twice with 15 mL phosphate buffer saline (PBS, 137 mM sodium chloride; 10 mM phosphate; 2.7 mM potassium chloride; pH 7.4). Ten mL of pathogens in PBS was added to each 6 cm diameter sterilized glass Petri dish containing various amounts of $\text{Ag-TiO}_2/\text{Fe}_3\text{O}_4$ and irradiated with visible fluorescence light (FL40S-N-EDL-NU, Mitsubishi/Osram, Japan, $\lambda > 420$ nm, 1040 lux) for various time intervals. The control groups were without photocatalyst. All control and experimental groups had 3 replicates. At each time interval, 20 μL of such solution was transferred from each Petri dish to 96-well plate containing 180 μL of 0.05% 2,3,5-triphenyl tetrazolium chloride (TTC) and incubated at 28°C for 10 hours. The absorbance of each tube at 540 nm was measured with ELISA reader after adding 50 μL of isopropanol to the tubes to terminate reaction [11].

The inhibition efficiencies to fish pathogen were calculated as

$$\frac{[\text{Abs}]_i - [\text{Abs}]_t}{[\text{Abs}]_i} \times 100\%, \quad (2)$$

where $[\text{Abs}]_i$ is the absorbance of control group at certain time interval and $[\text{Abs}]_t$ is the absorbance of experimental group at the same time interval.

FIGURE 1: XRD spectra of Ag-TiO₂/Fe₃O₄.

3. Results and Discussion

Figure 1 displays the XRD patterns of P25 TiO₂, Fe₃O₄, and Ag-TiO₂/Fe₃O₄. The main peaks of Ag-TiO₂/Fe₃O₄ are present at 25.3, 38, 48, and 54° corresponding to (101), (004), (200), and (211) planes of TiO₂, respectively (JCPDS, number 21-1272). With no evidence of its correspondence to the rutile phase, the patterns correspond to the anatase phase exclusively at the calcination temperature of 450°C. These results help to conclude that the presence of the iron oxide has no accelerating effect on the anatase-rutile phase transformation of the TiO₂. In addition, there is no characteristic peak of Ag presented in the pattern, which implies that the amount of Ag particles is not adequate to present their characteristic patterns [12, 13]. The pattern of Fe₃O₄ does not appear in the XRD, which may indicate that Fe₃O₄ is encapsulated by Ag-TiO₂. However, the broadened patterns suggest that Ag⁺ doping suppresses the growth of TiO₂ crystals.

The average crystallite size (D) of catalyst is estimated using Scherrer's equation:

$$D = \frac{k\lambda}{\beta \cos \theta}, \quad (3)$$

where D is crystallite size (nm), k is crystallite shape factor (0.90), λ is X-ray wavelength, for CuK α (0.15418 nm), β is the full-width-half-maximum (FWHM) of the peak, and θ is Bragg angle.

The crystallite size can be measured via the diffraction data in Figure 1 according to the Scherrer equation for the peak at 25.3°. The estimated size is about 12.53 nm.

Figure 2 shows the influence of Ag and Fe₃O₄ on the UV-Visible light absorption. Fe₃O₄ slightly enhances the visible light absorption of TiO₂. With the modification of Ag, the shifting of Ag-TiO₂ absorption spectrum to longer wavelengths is noticeable, which is due to the interaction between Ag and TiO₂ matrix. In addition, Ag-TiO₂/Fe₃O₄ demonstrates significantly higher absorption in the 400–800 nm range.

FIGURE 2: UV-Vis diffuse reflectance spectra for the as-synthesized samples.

TABLE 1: Estimated band gap energy of as-synthesized samples.

Sample	Band gap energy (eV)	Band edge wavelength (nm) ^a
TiO ₂ /Fe ₃ O ₄	2.9	428
Ag-TiO ₂	2.7	460
Ag-TiO ₂ /Fe ₃ O ₄	2.35	528

$$^a E_{bg} = hc/\lambda.$$

As shown in Figure 3, UV-Vis absorption spectra are converted to the Tauc plot of $(\alpha h\nu)^{1/2}$ and photon energy, and the linear extrapolations are made by drawing a tangent line through the maximum slope and taking its intersection with X-axis at $(\alpha h\nu)^{1/2} = 0$ [14].

The calculated energy band gaps of TiO₂/Fe₃O₄, Ag-TiO₂, and Ag-TiO₂/Fe₃O₄ are 2.9, 2.7, and 2.35 eV, respectively (Figure 3). Compared to the original anatase TiO₂ band gap of 3.2 eV, Fe₃O₄ and Ag dopants have improved the photocatalytic activity under visible light via narrowing the band gap and enhancing the visible light absorption of TiO₂ (Table 1).

Figure 4 shows the XPS spectra for Ag3d region of Ag-TiO₂/Fe₃O₄. The spectra consist of two peaks at around 367 and 373 eV, which correspond to Ag3d_{5/2} and Ag3d_{3/2}, respectively. The peaks are slightly broadened and can be considered as the sum of multiple overlapping peaks. As the XPS infers, the silver species on the Ag-TiO₂/Fe₃O₄ photocatalyst are metallic silver and silver ions coexisting in terms of the bonding energy corresponding to Ag3d_{5/2} of metallic Ag (Ag⁰, 368 eV), Ag₂O (Ag⁺, 367.5 eV), and AgO (Ag²⁺, 367 eV), respectively [15, 16].

Figure 5 shows the morphology of the sample under TEM. The Ag-TiO₂/Fe₃O₄ particle connects tightly to one another. The diameter of the particles is in the range of 14–40 nm.

Figure 6 displays the energy dispersive X-ray (EDX) spectra analysis of Ag-TiO₂/Fe₃O₄ and Table 2 lists the

FIGURE 3: Tauc plot for the determination of band gap for the as-synthesized samples.

FIGURE 4: X-ray photoelectron spectra (XPS) of the as-synthesized Ag-TiO₂/Fe₃O₄ in the Ag3d region.

composition of the prepared photocatalyst. Among the four elements (Ti, Fe, O, and Ag) presented, higher Ti content compared to magnetite could be resulting from the formation of TiO₂ layer coated on Fe₃O₄ particles. The Ag signals are around 2.8 keV, which may indicate the existence of Ag particles in catalyst.

Figure 7 displays the magnetic property of Ag-TiO₂/Fe₃O₄ measured at 25°C. The absence of hysteresis loop of the sample indicates the superparamagnetic character of the material [17]. Figure 8 shows the synthesized Ag-TiO₂/Fe₃O₄ (with a saturation magnetization of 2.7 emu/g) being recollected from the solution with a magnet.

Figure 9 shows the indigo carmine decolorization efficiency of TiO₂, Ag-TiO₂, TiO₂/Fe₃O₄, and Ag-TiO₂/Fe₃O₄, in visible light. Ag-TiO₂ exhibits the highest photocatalytic

FIGURE 5: TEM photograph for the as-synthesized Ag-TiO₂/Fe₃O₄.

FIGURE 6: Energy dispersive X-ray spectra for the as-synthesized Ag-TiO₂/Fe₃O₄.

TABLE 2: Characterization data of EDX for Ag-TiO₂/Fe₃O₄.

Element	Weight (%)	Atomic (%)
O K	26.55	54.12
Ti K	33.85	23.05
Fe K	38.59	22.53
Ag L	1.01	0.3
Total	100.00	

activity (near 100% indigo carmine degradation within 2 hours). No decolorization has been found in undoped TiO₂. The decolorization efficiencies of TiO₂/Fe₃O₄ and Ag-TiO₂/Fe₃O₄ are ~68% and ~85%, respectively, after 5 hours. The results suggest that Ag deposition has enhanced the visible light photocatalytic activity of TiO₂. Such enhancement may be attributed to the electron interaction at the contact between the metal deposits and the semiconductor surface. The Ag deposits act as e⁻ traps that immobilize the photogenerated electrons. The trapped electrons are then transferred to oxygen to form highly oxidative species such as O₂⁻. The Fe₃O₄ in the photocatalyst helps to enhance the visible light activity of TiO₂. As TiO₂ is the active site of the catalyst, substituting Ag-TiO₂ with Fe₃O₄ may decrease the photocatalytic activity. Although Ag-TiO₂ demonstrates higher decolorization efficiency than Ag-TiO₂/Fe₃O₄, yet Ag-TiO₂ is not collectable with magnet after dispersing in

FIGURE 7: Magnetization curves of Ag-TiO₂/Fe₃O₄ at room temperature.

FIGURE 8: Photographs of Ag-TiO₂/Fe₃O₄ dispersed in water after sonication (a) along with its response to the presence of magnet at 10 seconds (b), 1 minute (c), and 5 minutes (d).

FIGURE 9: Photocatalytic activity in decolorization of indigo carmine (O.D.620 = 0.1) under visible light irradiation at room temperature.

water. As a result, only Ag-TiO₂/Fe₃O₄ is used for bactericidal efficiency evaluation.

The catalyst reusability is an important parameter for practical applications. The repetitive use of as-synthesized Ag-TiO₂/Fe₃O₄ was studied for different cycles of indigo carmine decolorization under visible light irradiation. The catalyst was recovered using a permanent magnet bar and used for three cycles with all other parameters kept constant. The results demonstrate that Ag-TiO₂/Fe₃O₄ maintains good activity in three runs, with only a small loss. The drop in decolorization might be due to the loss or aggregation of the particles during the recycling process. The decolorization after 6 h irradiation at the third run (Figure 10) was around 85%, which indicates that Ag-TiO₂/Fe₃O₄ sustains well from recycling and has good potential for practical applications.

The research team tested three Ag-TiO₂/Fe₃O₄ loadings (i.e., 3.5 mg, 2.7 mg, and 1.8 mg) to select its suitable one in 10 mL of phosphate buffer saline (PBS) containing fish pathogens. As displayed in Figure 11, the antibacterial efficiencies are less than 10% in all loadings for all catalysts within the first 30 minutes. After that, the specimen of 3.5 mg Ag-TiO₂/Fe₃O₄ load demonstrates sharp efficiency increase to reach ~100% after 90 minutes. The specimen of 2.7 mg load demonstrates increased antibacterial efficiency after 60 minutes to reach 95% after 120 minutes. The specimen of 1.8 mg load demonstrates very low antibacterial efficiency, only 18% fish pathogens degradation. Therefore, 2.7 mg load was chosen for further study.

The experiment uses *Aeromonas hydrophila* (BCRC-13018), *Edwardsiella tarda* (BCRC10670), and *Photobacterium damsela* subsp. *piscicida* (BCRC17065) as target bacteria. These bacteria, which cause losses in wild and farmed fish stocks, are gram negative fish pathogens that inhabit in freshwater as well as seawater. As shown in Figure 12, the effects have been slow in the first 30 minutes and then start to increase more significantly. Almost all bacteria were

FIGURE 10: The reusability of Ag-TiO₂/Fe₃O₄ as demonstrated in decolorization of indigo carmine under visible light irradiation.

destroyed by Ag-TiO₂/Fe₃O₄ after 120 minutes irradiation. The bactericidal efficiency is about 20% for both BCRC13018 and BCRC17065 after 60 minutes of visible light irradiation. No significant difference has been found between these two pathogens. After 120 minutes, the bactericidal efficiencies increase to 93% for BCRC13018 and 81% for BCRC17065. The results suggest that *Photobacterium damsela* subsp. *piscicida* is more resistant to Ag-TiO₂/Fe₃O₄ among these three pathogens.

Figure 13 shows that in the dark, where no photocatalysis process occurs, *Aeromonas hydrophila* and *Photobacterium damsela* subsp. *piscicida* degrade ~15% after 120 minutes, while *Edwardsiella tarda* degrades more quickly and reach 100% within 120 minutes. The bactericide effect seems to be exclusive due to the presence of Ag⁺. Such findings indicate that *Edwardsiella tarda* is a very sensitive microorganism and more susceptible to silver particle. These results suggest that Ag-TiO₂/Fe₃O₄'s photocatalytic bactericidal effect is species dependent.

4. Conclusions

Ag-TiO₂/Fe₃O₄ magnetic photocatalyst has demonstrated strong antimicrobial properties through a mechanism including photocatalytic production of reactive oxygen species

FIGURE 11: Photocatalytic bactericidal efficiency for *Aeromonas hydrophila* (BCRC13018) at different loadings of Ag-TiO₂/Fe₃O₄ under visible light irradiation.

FIGURE 12: Bactericidal efficiency of 2.7 mg Ag-TiO₂/Fe₃O₄ to *Aeromonas hydrophila* (◆), *Edwardsiella tarda* (▲), and *Photobacterium damsela subsp. piscicida* (■) under visible light.

that damage cell components and viruses [18]. The holes on the valence band of TiO₂ can react with either H₂O or OH⁻ absorbed on the surface to produce hydroxyl radicals and with the electrons on the conduction band to reduce O₂ to produce superoxide anion. The detection of other reactive oxygen species such as H₂O₂ and singlet oxygen has also been reported. Hydroxyl radical and superoxide anions, both known to be highly reactive with biological samples, are considered the main species generated in the anodic and cathodic pathways, respectively, of photocatalytic processes in the presence of oxygen. The XPS data indicated different silver species coexisting in the Ag3d_{5/2} region of

FIGURE 13: Bactericidal efficiency of 2.7 mg Ag-TiO₂/Fe₃O₄ to *Aeromonas hydrophila* (■), *Edwardsiella tarda* (▲), and *Photobacterium damsela subsp. piscicida* (◆) in the dark.

photocatalyst with binding energies at around 367 eV and 368 eV, assigned to silver ion (Ag⁺ and/or Ag²⁺) and metallic silver (Ag⁰), respectively. Ag⁺ can cause severe alterations to bacteria via binding to bacterial denatured DNA and RNA so as to inhibit the replication. The modifications of membrane structure that include changes in membrane-bound enzyme activities, metabolic pathways, transport systems, and permeability alterations lead to cell death. Ag⁺ from Ag-TiO₂ inactivates membrane proteins and respiratory enzymes. Reactive oxygen species damage cell membrane when cell comes into contact with catalyst surface. Ag also acts as the trap of photogenerated electrons to prevent the e⁻-h⁺ pairs from recombining rapidly after photoexcitation.

As a final remark, the research team intend to use light emitting diodes (LEDs) of different colors as the light source to identify the most responsive spectrum of Ag-TiO₂/Fe₃O₄ for the future study since high intensity LEDs have become prominent light sources for scientific research [19–21].

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] V. S. Blazer, "Bacterial fish pathogens," *Environmental Biology of Fishes*, vol. 21, no. 1, pp. 77–79, 1988.
- [2] L. Novotny, L. Dvorska, A. Lorencova, V. Beran, and I. Pavlik, "Fish: a potential source of bacterial pathogens for human beings," *Veterinarni Medicina*, vol. 49, no. 9, pp. 343–358, 2004.
- [3] Z. Zhang and J. Gamage, "Applications of photocatalytic disinfection," *International Journal of Photoenergy*, vol. 2010, Article ID 764870, 11 pages, 2010.
- [4] K. S. Yao, T. C. Cheng, S. J. Li et al., "Comparison of photocatalytic activities of various dye-modified TiO_2 thin films under visible light," *Surface and Coatings Technology*, vol. 203, no. 5–7, pp. 922–924, 2008.
- [5] W. Choi, A. Termin, and M. R. Hoffmann, "The role of metal ion dopants in quantum-sized TiO_2 : correlation between photoreactivity and charge carrier recombination dynamics," *Journal of Physical Chemistry*, vol. 98, no. 51, pp. 13669–13679, 1994.
- [6] M. Maeda and T. Yamada, "Photocatalytic activity of metal-doped titanium oxide films prepared by sol-gel process," *Journal of Physics: Conference Series*, vol. 61, no. 1, article 151, pp. 755–759, 2007.
- [7] Q. L. Feng, J. Wu, G. Q. Chen, F. Z. Cui, T. N. Kim, and J. O. Kim, "A mechanistic study of the anti-bacterial effect of silver ions on *Escherichia coli* and *Staphylococcus aureus*," *Journal of Biomedical Materials Research*, vol. 52, pp. 662–668, 2000.
- [8] W. Wu, Q. He, and C. Jiang, "Magnetic iron oxide nanoparticles: synthesis and surface functionalization strategies," *Nanoscale Research Letter*, vol. 3, no. 11, pp. 397–415, 2008.
- [9] B. Tural, N. Özkan, and M. Volkan, "Preparation and characterization of polymer coated superparamagnetic magnetite nanoparticle agglomerates," *Journal of Physics and Chemistry of Solids*, vol. 70, no. 5, pp. 860–866, 2009.
- [10] Q. He, Z. Zhang, J. Xiong, Y. Xiong, and H. Xiao, "A novel biomaterial— $\text{Fe}_3\text{O}_4\text{:TiO}_2$ core-shell nano particle with magnetic performance and high visible light photocatalytic activity," *Optical Materials*, vol. 31, no. 2, pp. 380–384, 2008.
- [11] T. C. Cheng, K. S. Yao, N. Yeh et al., "Bactericidal effect of blue LED light irradiated $\text{TiO}_2/\text{Fe}_3\text{O}_4$ particles on fish pathogen in seawater," *Thin Solid Films*, vol. 519, no. 15, pp. 5002–5006, 2011.
- [12] S. A. Amin, M. Pazouki, and A. Hosseinnia, "Synthesis of TiO_2 -Ag nanocomposite with sol-gel method and investigation of its antibacterial activity against *E. coli*," *Powder Technology*, vol. 196, no. 3, pp. 241–245, 2009.
- [13] K. Loganathan, P. Bommusamy, P. Muthaiahpillai, and M. Velayutham, "The syntheses, characterizations, and photocatalytic activities of silver, platinum, and gold doped TiO_2 nanoparticles," *Environmental Engineering Research*, vol. 16, no. 2, pp. 81–90, 2011.
- [14] E. Kanchanatip, N. Grisdanurak, R. Thongruang, and A. Neramittagapong, "Degradation of paraquat under visible light over fullerene modified V- TiO_2 ," *Reaction Kinetics, Mechanisms and Catalysis*, vol. 103, no. 1, pp. 227–237, 2011.
- [15] I. M. Arabatzis, T. Stergiopoulos, M. C. Bernard, D. Labou, S. G. Neophytides, and P. Falaras, "Silver-modified titanium dioxide thin films for efficient photodegradation of methyl orange," *Applied Catalysis B: Environmental*, vol. 42, no. 2, pp. 187–201, 2003.
- [16] P. Prieto, V. Nistor, K. Nouneh, M. Oyama, M. Abd-Lefdil, and R. Diaz, "XPS study of silver, nickel and bimetallic silver-nickel nanoparticles prepared by seed-mediated growth," *Applied Surface Science*, vol. 258, no. 22, pp. 8807–8813, 2012.
- [17] Z. Teng, X. Su, G. Chen et al., "Superparamagnetic high-magnetization composite microspheres with $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core and highly crystallized mesoporous TiO_2 shell," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 402, pp. 60–65, 2012.
- [18] Q. Li, S. Mahendra, D. Y. Lyon et al., "Antimicrobial nanomaterials for water disinfection and microbial control: potential applications and implications," *Water Research*, vol. 42, no. 18, pp. 4591–4602, 2008.
- [19] N. Yeh and J.-P. Chung, "High-brightness LEDs-Energy efficient lighting sources and their potential in indoor plant cultivation," *Renewable and Sustainable Energy Reviews*, vol. 13, no. 8, pp. 2175–2180, 2009.
- [20] N. G. Yeh, C.-H. Wu, and T. C. Cheng, "Light-emitting diodes—their potential in biomedical applications," *Renewable and Sustainable Energy Reviews*, vol. 14, no. 8, pp. 2161–2166, 2010.
- [21] N. Yeh, P. Yeh, N. Shih, O. Byadgi, and T. C. Cheng, "Applications of light-emitting diodes in researches conducted in aquatic environment," *Renewable and Sustainable Energy Reviews*, vol. 32, pp. 611–618, 2014.