Ultrasound-Assisted Synthesis of Nonmetal-Doped Titanium Dioxide Photocatalysts for Simultaneous H2 Production and Chemical Oxygen Demand Removal from Industrial Wastewater

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ABSTRACT: A series of nonmetal-doped titanium dioxide (Nm/\(\text{TiO}_2\), where \(x\) is the weight fraction of nonmetal elements) photocatalysts was prepared via ultrasonic-assisted impregnation for simultaneous hydrogen (H\(_2\)) production and chemical oxygen demand (COD) removal from industrial wastewater. Three types of Nm elements, carbon (C), silicon (Si), and phosphorus (P), were explored. The P\(_1/\text{TiO}_2\) exhibited a higher photocatalytic activity for H\(_2\) production and COD removal than the C\(_1/\text{TiO}_2\) and Si\(_1/\text{TiO}_2\) photocatalysts. Approximately 6.43 mmol/g photocatalyst of H\(_2\) was produced, and around 26% COD removal was achieved at a P\(_1/\text{TiO}_2\) loading of 4.0 g/L, a light intensity of 5.93 mW/cm\(^2\), and a radiation time of 4 h. This is because the P\(_1/\text{TiO}_2\) photocatalyst exhibited lower point of zero charge values and a more appropriate band position compared with other Nm\(_x/\text{TiO}_2\) photocatalysts to produce H\(^+\), which can consequently form H\(_2\), and reactive oxygen species (HO\(^-\) and O\(_2\)\(^-\)), which serve as oxidizing agents to degrade the organic pollutants. Increasing the content of the P element doped into the TiO\(_2\)-based material up to 7.0% by weight enhanced the H\(_2\) production and COD removal up to 8.34 mmol/g photocatalyst and 50.6%, respectively. This is attributed to the combined effect of the point of zero charge value and the \(S_{\text{BET}}\) of the prepared photocatalysts. The photocatalytic activity of the P\(_7/\text{TiO}_2\) photocatalyst was still higher than the TiO\(_2\)-based material after the fourth use.

1. INTRODUCTION

Due to the problems of global warming and poor air quality that are associated with greenhouse gases (GHG) and particulates emitted from fossil fuel combustion, together with the fast depletion of nonrenewable fossil-based energy sources, a number of research studies have been conducted to develop more eco-friendly energy sources.\(^1,2\) Currently, hydrogen (H\(_2\)) is considered as an environmentally friendly energy carrier for the near future development due to its toxic-free emission and high energy capacity.\(^3\) In addition, it is widely used in various sectors, such as transportation, industries, and residences.\(^4\) For example, it is used as a hydrogenating agent in industrial processes, as a direct feed to fuel cells to produce electricity, and also as a feedstock for internal combustion engines, for turbines, and thermal energy.\(^4\) Almost all H\(_2\) is currently produced from carbon-based materials, such as natural gas via steam reforming (\(\sim 50\)%), oil/naphtha reforming (\(\sim 30\)%), coal gasification (\(\sim 18\)%), and other sources (\(\sim 2\)%), which leads to massive emissions of GHG\(^2\). Within the next decade, the steam reforming of natural gas and catalytic biomass gasification will still be the principal processes to produce H\(_2\). However, in the future, it is believed that the massive transition of H\(_2\) production from fossil resources (current stage) will be complemented with H\(_2\) produced from biomass (midterm stage) and finally green H\(_2\) from renewable resources (e.g., water and sunlight) by the year 2050.\(^4\) Thus, many research activities have been performed to develop a clean and environmentally benign method for producing H\(_2\) from renewable feedstocks in order to achieve a zero-carbon footprint in all sectors.

Based on various H\(_2\) production processes, water splitting using a photocatalyst is a promising environmental benign process to produce H\(_2\) from water and sunlight. This process involves the dissociation of water (H\(_2\)O) molecules to H\(_2\) and oxygen (O\(_2\)) by the generated electron (e\(^-\))−hole (h\(^+\)) pairs in a semiconductor when it absorbs appropriate energetic light.\(^5,6\) Currently, the most utilized photocatalyst is titanium dioxide (TiO\(_2\)) due to its low cost, high photochemical and thermal stability, and environmentally friendly nature.\(^7,8\) However, its wide bandgap (\(\sim 3.2\) eV) and fast rate of e\(^-\)−h\(^+\) recombination

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serve to limit its applications under visible light, which lower its photocatalytic activity.

Many strategies have been attempted to shorten the bandgap energy of TiO$_2$ to promote more visible-light absorption and slow down the rate of e$^−$−h$^+$ recombination of TiO$_2$. These include the modification of the TiO$_2$ structure by metal doping, nonmetal (Nm) doping, and coupling with other semiconductors, as well as tuning oxygen defects. Moreover, in order to mitigate the fast rate of e$^−$−h$^+$ recombination, various organic and inorganic substances have been extensively used as h$^+$ scavengers (or e$^−$ donors), such as organic compounds (e.g., alcohols, amine compounds, organic acids, etc.), inorganic compounds (e.g., sodium sulfide and sodium sulﬁte mixtures), and paper. These added substances are able to react irreversibly with the photogenerated h$^+$, leaving the strong reducing photogenerated e$^−$ to react with H$^+$ to form H$_2$ molecules.

For the purpose of green energy production and environmental remediation, the utilization of organic and/or inorganic substances in wastewater as h$^+$ scavengers instead of synthetic chemical addition is beneﬁcial in terms of both economic and environmental points of view. This is because in addition to H$_2$ being produced via a green process, the pollutant level in the wastewater is reduced in the photocatalytic process. Therefore, many attempts have focused on the production of H$_2$ by a photocatalytic process from various wastewaters such as those from glycerol, ammonia, palm oil mill, olive mill, fruit juice, and sulfor in the photocatalytic process. Being produced via a green process, the pollutant level in the wastewater is reduced in the photocatalytic process.

2. RESULTS AND DISCUSSION

2.1. Effect of Pollutant Loading. As mentioned previously, the organic molecules in wastewater can act as the h$^+$ scavengers or e$^−$ donors and so can prolong the e$^−$−h$^+$ pair life as well as the photocatalytic activity. Prior to the photocatalytic reaction, they must be properly adsorbed onto the photocatalyst surface under a dark condition. Thus, the appropriate pollutant loading should be determined to get an effective operating condition since a too low pollutant loading would give ineffective e$^−$−h$^+$ separation, while a too high pollutant loading may saturate the surface of the photocatalyst and become a shading barrier to absorb the photon energy from irradiated light leading to a low photocatalytic efficiency.

In this study, the pollutant loading was designed as a function of the COD level as a high COD level (7322 ± 736 mg/L, obtained from pretreated wastewater) and a low COD level (1574 ± 275 mg/L obtained from a dilution of the pretreated wastewater). As shown in Figure 1, the wastewater with a high COD level provided a higher quantity of H$_2$ production and COD removal for all selected photocatalysts. This might be attributed to the presence of adequate organic molecules in the high COD level-containing wastewater, to attach to the generated h$^+$ in the VB and consequently slow down the rate of e$^−$−h$^+$ recombination.

2.2. Effect of the Type of Doped Nm. Using ultrasound-assisted impregnation facilitated the decoration of each of the C, Si, and P Nm elements into the calcined TiO$_2$ (Figure 2) to a final level close to the target value (Table 1). Doping of the respective Nm element into TiO$_2$ did not markedly affect the crystal phases and structures of TiO$_2$, as seen in Figure 3a. All the Nm$_i$/TiO$_2$ photocatalysts exhibited almost similar XRD peaks, which were the main characteristic peaks of the calcined TiO$_2$-based material. That is, they exhibited the characteristic peaks of the anatase phase at 20 angles of 25.30, 37.91, 48.00, 50.00, 55.04, 62.67, 68.87, 70.31, and 75.07°, related to the crystal planes of A(101), A(004), A(200), A(105), A(221), A(204), A(116), A(220), and A(215), respectively. In addition, they also displayed the three characteristic peaks of TiO$_2$ in the rutile phase at 20 angles of 27.37 and 36.08°, corresponding to the crystal planes of R(110) and R(101), respectively.

Figure 1. Effect of wastewater concentrations on H$_2$ production and COD removal using the TiO$_2$ and Nm$_i$/TiO$_2$ photocatalysts at a loading of 4.0 g/L, a light intensity of 5.93 mW/cm$^2$, and an irradiation time of 4 h.

Figure 4. Improvement of the Nm$_i$/TiO$_2$ photocatalysts to exhibit a higher UV light absorption capacity than that of the calcined TiO$_2$ at identical wavelengths ($\lambda$ < 415 nm), but they cannot promote visible-light adsorption ($\lambda$ > 415 nm). This is not the case for the P$_i$/TiO$_2$ photocatalyst because it exhibited an obvious visible-light absorption ability at wavelengths above 415 nm. Quantitatively, according to the
The Tauc plot, the explicit values of the bandgap energy of the TiO2, C1/TiO2, Si1/TiO2, and P1/TiO2 photocatalysts were 3.32, 3.21, 3.26, and 3.22 eV, respectively. According to the XPS analysis, all Nm1/TiO2 demonstrated the spectra of O 1s, Ti 2p, and C 1s peaks of O, Ti, and C (from carbon tape) (Figure 5a). In addition, Figure 5b displays the Si 2s and P 2p peaks of Si and P at binding energies of 99.7 and 135 eV, respectively. The presence of the C 1s peak of C was overlaid with that of carbon tape. Nevertheless, the peaks can indicate the replacement of the O atomic lattices by the doped C, Si, or P elements, which usually affected the effects of the electronic structure of the TiO2-based material.47,49 That is, the doped elements can cause the formation of an interstage energy level above the VB edge of TiO2 (O in 2p). The excitation of electrons from this interstage energy level to the conductance band (CB) induces the redshift of UV−vis spectra.50 Typically, the interstage energy level of the bands introduced by the Nm dopants increased with decreasing electronegativity.51 In this case, the electronegativities of the C, Si, and P elements were 2.5, 1.8, and 2.1, respectively, so the distance of the interstage energy level with respect to the VB was ranked in the order of Si > P > C. Too short or too long distance between the interstage energy level and the VB may lessen the capability of electron excitation from the VB to the interstage level and/or from the interstage level to the CB. The P1/TiO2 photocatalyst exhibited a greater redshift than the other prepared photocatalysts, which is probably due to its more appropriate interstage energy level. In addition, at a low binding energy, the TiO2, C1/TiO2, Si1/TiO2, and P1/TiO2 photocatalysts exhibited the maximum edge position of the VB at energies of around 2.60, 3.00, 1.89, and 2.43 eV, respectively (Figure 6). This indicated that the minimum CB of the respective prepared photocatalysts would occur at −0.72, −0.21, −1.37, and −0.79 eV. Interestingly, the valence band XPS spectra of Si1/TiO2 and P1/TiO2 exhibited additional diffusive electronic states above the valence band edge of the.

**Table 1. Properties of the Prepared Photocatalysts**

| type of photocatalyst | target content (wt %) | actual contenta (wt %) | anatase contentb (%) | crystal size (nm)c | bandgap energyd (eV) | PZC | S BET (m2/g) |
|----------------------|-----------------------|------------------------|----------------------|------------------|----------------------|-----|--------------|
| TiO2                 | 90.12                 | 22.19                  | 3.32                 | 6.77             | 83.19                |     |              |
| C1/TiO2              | 1.0                   | 1.44 ± 0.09            | 91.10                | 21.98            | 3.21                 | 5.83 | 78.41        |
| Si1/TiO2             | 1.0                   | 0.98 ± 0.03            | 90.85                | 22.06            | 3.26                 | 4.65 | 55.48        |
| P1/TiO2              | 1.0                   | 0.98 ± 0.01            | 91.92                | 21.75            | 3.22                 | 2.98 | 79.38        |
| P3/TiO2              | 3.0                   | 3.22 ± 0.02            | 91.09                | 22.03            | 3.22                 | 2.39 | 57.83        |
| P5/TiO2              | 5.0                   | 4.91 ± 0.02            | 91.18                | 22.45            | 3.22                 | 2.23 | 46.79        |
| P7/TiO2              | 7.0                   | 6.88 ± 0.02            | 91.56                | 22.84            | 3.22                 | 2.19 | 45.02        |
| P9/TiO2              | 9.0                   | 9.31 ± 0.03            | 91.39                | 22.66            | 3.22                 | 2.15 | 44.57        |

a Estimated from the SEM-EDS analysis. b Calculated from the A(101) and R(110) peaks of the XRD pattern using the Spurr and Myers equation. c Calculated from the A(101) peak of the XRD pattern using the Debye and Scherrer equation. d Calculated from the UV−vis spectra using the Tauc equation.
TiO2-based material. These confirmed the presence of mid-band states coming from the fulfillment of Si and P species as impurities above the VB. A similar feature was also reported in the C-, S-, and N-doped TiO2. The band position of the Nm1/TiO2 photocatalysts was roughly sketched (Scheme 1).

It is well-known that the dark adsorption of active substances proceeds with the photocatalytic reaction. The quality and quantity of absorbed molecules depend upon the relationship between the PZC of the photocatalytic materials and the pH of the aqueous medium. Due to electrostatic interactions, when the solution pH is higher than the PZC value, the photocatalyst exhibits negative charges, which strongly prefer to adsorb cationic molecules. However, when the solution pH is lower than the PZC value, the photocatalyst is positively charged and readily adsorbs anionic molecules. In practical operation, a solution pH close to the PZC value will induce aggregation of photocatalyst nanoparticles (NPs) due to the reduced electrostatic repulsion among the solid NPs within the liquid. This, consequently, reduced the photocatalytic efficiency through the reduction of the exposed surface area and the shading effect.

As demonstrated in Figure 7a, all the photocatalysts exhibited a buffer behavior during the initial pH of 4. The P1/TiO2 exhibited the lowest PZC compared to the TiO2 and other Nm1/TiO2 photocatalysts (Table 1). This might be attributed to the surface modification of TiO2 via the (PO4)3− which can induce the formation of a large number of negatively charged sites, resulting in the marked decrease in the PZC value as well as prolongation of the lifetime of photogenerated charge carriers and also the improvement of the photocatalytic performance.

For the textural properties, shown in Figure 9, the Nm1/TiO2 photocatalysts exhibited typical H4-shaped hysteresis loops of mesoporous materials, similar to those of M/TiO2, where M is various decorated metals, including Ni, Au, Pt, and Pd, and S/TiO2, where S is a semiconductor, including Bi2O3, Nb2O5, and WO3. Moreover, all the Nm1/TiO2 photocatalysts exhibited a buffer behavior during the initial pH of 4. The P1/TiO2 exhibited the lowest PZC compared to the TiO2 and other Nm1/TiO2 photocatalysts (Table 1). This might be attributed to the surface modification of TiO2 via the (PO4)3−, which can induce the formation of a large number of negatively charged sites, resulting in the marked decrease in the PZC value as well as prolongation of the lifetime of photogenerated charge carriers and also the improvement of the photocatalytic performance. From the effect of the three Nm types (C, Si, and P) on the qualitative rate of e−−h+ recombination, the PL analysis was then performed over a wavelength range of 350–550 nm. As shown in Figure 8, three sharp peaks of PL spectra of all photocatalysts appeared at the wavelengths of 420, 486, and 530 nm, representing the backward transfer of electrons from the CB to the VB. Among all prepared Nm1/TiO2, only the P1/TiO2 exhibited an intensity lower than that of the TiO2-based material, indicating its lower e−−h+ recombination rate compared with other Nm1/TiO2.

For the textural properties, shown in Figure 9, the Nm1/TiO2 photocatalysts exhibited typical H4-shaped hysteresis loops of mesoporous materials, similar to those of M/TiO2, where M is various decorated metals, including Ni, Au, Pt, and Pd, and S/TiO2, where S is a semiconductor, including Bi2O3, Nb2O5, and WO3. Moreover, all the Nm1/TiO2 photocatalysts exhibited a buffer behavior during the initial pH of 4. The P1/TiO2 exhibited the lowest PZC compared to the TiO2 and other Nm1/TiO2 photocatalysts (Table 1). This might be attributed to the surface modification of TiO2 via the (PO4)3−, which can induce the formation of a large number of negatively charged sites, resulting in the marked decrease in the PZC value as well as prolongation of the lifetime of photogenerated charge carriers and also the improvement of the photocatalytic performance. From the effect of the three Nm types (C, Si, and P) on the qualitative rate of e−−h+ recombination, the PL analysis was then performed over a wavelength range of 350–550 nm. As shown in Figure 8, three sharp peaks of PL spectra of all photocatalysts appeared at the wavelengths of 420, 486, and 530 nm, representing the backward transfer of electrons from the CB to the VB. Among all prepared Nm1/TiO2, only the P1/TiO2 exhibited an intensity lower than that of the TiO2-based material, indicating its lower e−−h+ recombination rate compared with other Nm1/TiO2.
photocatalysts exhibited a lower BET surface area ($S_{BET}$) than the original TiO$_2$ (Table 1). This was attributed to the partial loss of the TiO$_2$ surface area caused by occupation of the doped Nm elements. However, the C$_x$/TiO$_2$ and P$_x$/TiO$_2$ photocatalysts exhibited comparable $S_{BET}$ values of 78−79 m$^2$/g, which were higher than that of the Si$_x$/TiO$_2$ photocatalyst. This might be attributed to the large atomic size of Si (1.11 Å) compared with C (0.67 Å) and P (0.80 Å), and so, it required a large contact surface area.

Figure 6. Representative XPS spectra at a low range of binding energy of the Nm$_1$/TiO$_2$ photocatalysts.

Scheme 1. Sketch of the Band Position of the Nm$_1$/TiO$_2$ Photocatalysts with 5.93 mW/cm$^2$ for 4 h

Figure 7. Relationship between the initial and final pH of (a) Nm$_1$/TiO$_2$ and (b) P$_x$/TiO$_2$ photocatalysts.

Figure 8. PL spectra of all photocatalysts with peaks appearing at wavelengths of 420, 486, and 530 nm.

Figure 9. Representative N$_2$ physisorption isotherm and (inset) pore size distribution of the P$_1$/TiO$_2$ photocatalyst.

Figure 10a displays the photocatalytic activity of all the prepared Nm$_1$/TiO$_2$ photocatalysts, in terms of the simultaneous H$_2$ production and COD removal, from pretreated-
In the presence of organic substances, the HO, O2−, and h+ are able to degrade the contained substances to form various intermediate species. 45,58 Generally, the types of generated intermediate species depend upon the type of organic substance. For example, the RCH2O−, RCH2O, RCHOH, RCHO, [R’COOH]−, and H+ can be generated if glucose (RCH2OH or R’CH2OH) is used as the source of organic molecules. 58 The generated H+ is readily reduced via the photogenerated e− according to reaction R5 to form H2, while the generated intermediate species can be further oxidized to form lower-molecular-weight intermediate species, as well as CO2 in the case of complete oxidation, as shown in reactions R6–R8.

\[ \text{HO}^+ + \text{organic substances} \rightarrow \text{intermediate} + \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2 \]  
\[ \text{O}_2^{*-} + \text{organic substances} \rightarrow \text{intermediate} + \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2 \]  
\[ \text{h}^+ + \text{organic substances} \rightarrow \text{intermediate} + \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2 \]  

Based on all the above-mentioned reactions, a high quantity of the produced oxidizing agent can promote a high reforming efficiency of organic substances. This was typically based on the band position of the prepared Nm1/TiO2 photocatalysts. According to the sketch of the band position of the Nm1/TiO2 photocatalysts (Scheme 1), the TiO2 and P1/TiO2 photocatalysts exhibited a higher positive VB position than the oxidation potential of H2 to HO radicals and also displayed a more negative CB position than the reduction potential of O2 to O2− radicals. Thus, both HO and O2− radicals would be formed in the presence of either photocatalyst and were effective to degrade pollutant molecules. A high COD removal level was observed via the P1/TiO2 photocatalyst compared with TiO2 due to its shorter bandgap energy to absorb a high quantity of light. However, only the HO radicals could be produced in the presence of C1/TiO2, while only the O2− radicals could be generated in the presence of Si1/TiO2. The high COD removal level by the C1/TiO2 photocatalyst was due to the fact that HO radicals have a stronger oxidizing power than O2− radicals. For the H2 production, the bottom of the CB was more negative than the reduction potential of H+ in all the photocatalysts, indicating their ability to produce H2 via the photocatalytic reaction. The quantity of H2 produced was greater with P1/TiO2 than with Si1/TiO2, which was probably due to its shorter bandgap energy. The C1/TiO2 exhibited a lower H2 production than the P1/TiO2 even though it exhibited a shorter bandgap energy. The C1/TiO2 exhibited a lower H2 production than the P1/TiO2 even though it exhibited a shorter bandgap energy. The C1/TiO2 exhibited a lower H2 production than the P1/TiO2 even though it exhibited a shorter bandgap energy. The C1/TiO2 exhibited a lower H2 production than the P1/TiO2 even though it exhibited a shorter bandgap energy. The C1/TiO2 exhibited a lower H2 production than the P1/TiO2 even though it exhibited a shorter bandgap energy. The C1/TiO2 exhibited a lower H2 production than the P1/TiO2 even though it exhibited a shorter bandgap energy. The C1/TiO2 exhibited a lower H2 production than the P1/TiO2 even though it exhibited a shorter bandgap energy. The C1/TiO2 exhibited a lower H2 production than the P1/TiO2 even though it exhibited a shorter bandgap energy. The C1/TiO2 exhibited a lower H2 production than the P1/TiO2 even though it exhibited a shorter bandgap energy. The C1/TiO2 exhibited a lower H2 production than the P1/TiO2 even though it exhibited a shorter bandgap energy.

biodiesel wastewater in the presence of a 4.0 g/L photocatalyst loading and UV irradiation at 5.93 mW/cm2 for 4 h. All the Nm1/TiO2 photocatalysts exhibited a higher H2 production than the TiO2-based material and were ranked in the order of P1/TiO2 > Si1/TiO2 > C1/TiO2. Both C1/TiO2 and P1/TiO2 exhibited a higher COD removal level than TiO2, while Si1/TiO2 provided a broadly comparable level of COD removal. Here, it seems that only the PZC value played a role in either H2 production or COD removal.

In the photocatalytic process, when the photocatalyst absorbs light with a photon energy equal to or higher than its bandgap energy, the electron is excited from the VB to the CB, leaving a h+ at the VB. 5 Subsequently, several reactions can proceed via the photogenerated h+ and e− depending on their redox potentials. The generated h+ is able to oxidize H2O to form superoxide radicals (O2−) and hydrogen peroxide (H2O2) at potentials of +0.28 V/NHE and +1.23 V/NHE (pH 7) as reactions R1 and R2, respectively. In the meantime, the photogenerated e− is able to oxidize H2O to the hydroxyl radicals (HO·) to HO and O2 together with photons (H+) at potentials of +2.27 and +1.23 V/NHE (pH 7) as reactions R3 and R4, respectively. In addition, the photogenerated e− can react with the H+ generated from H2O dissociation with h+ to form H2 according to reaction R5.

\[ \text{H}_2\text{O} + \text{h}^+ \rightarrow \text{HO}^+ + \text{H}^+ \quad (E^0 = +2.27/V/NHE, \text{pH } 7) \]  
\[ \text{H}_2\text{O} + \text{h}^+ \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ \quad (E^0 = +1.23/V/NHE, \text{pH } 7) \]  
\[ \text{O}_2 + \text{e}^- \rightarrow \text{O}_2^{*-} \quad (E^0 = -0.28/V/NHE, \text{pH } 7) \]  
\[ \text{O}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 \quad (E^0 = +0.28/V/NHE, \text{pH } 7) \]  
\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (E^0 = 0/V/NHE, \text{pH } 7) \]

Figure 10. Effect of (a) nonmetal types (Nm1/TiO2) and (b) phosphorus loading levels (P1/TiO2 x = 1, 3, 5, 7, and 9 wt %) on the simultaneous H2 production and COD removal from the pretreated-biodiesel wastewater via photocatalysis with a 4.0 g/L photocatalyst and a light intensity of 5.93 mW/cm2 for 4 h.
transfer of e⁻ and h⁺ to the adjacent NPs as well as a prolongation of the e⁻−h⁺ lifetime. In summary, the H₂ production process together with the decontamination mechanism can be roughly proposed as the Scheme 2.

Scheme 2. Sketch of H₂ Production and Decontamination Mechanisms in Wastewater

2.3. Effect of the P Loading. To enhance the photocatalytic activity of P/TiO₂ for simultaneous H₂ production and COD removal, different contents of P were doped into the structure of the TiO₂-based materials via ultrasound-assisted impregnation. As shown in Table 1, the actual P element contents in the respective Pₓ/TiO₂ photocatalysts, as measured using SEM-EDS analysis, were close to the target weight content. Doping different amounts of the P element did not alter the crystal structure of the calcined TiO₂ (Figure 3b) nor the bandgap energy, which remained at 3.22 eV (Figure 4), suggesting that doping with the P element at up to 9.0 wt % did not affect the internal structure and optical property of the Pₓ/TiO₂ photocatalysts. However, increasing the content of the P element doped into the calcined TiO₂ increased the amount of surface negative charges on the TiO₂ and led to a marked decrease in the PZC value (Figure 7 and Table 1). With respect to the textural properties, all the prepared Pₓ/TiO₂ photocatalysts exhibited typical H4-shaped hysteresis loops of mesoporous materials (figure not shown). However, increasing the amount of the doped P element on the TiO₂-based material reduced the S BET of the Pₓ/TiO₂ photocatalysts. The photocatalytic activity of the Pₓ/TiO₂ photocatalyst for simultaneous H₂ production and COD removal is summarized in Figure 10b. All the Pₓ/TiO₂ photocatalysts were clearly more effective in producing H₂ simultaneously with COD removal compared with calcined TiO₂. Increasing the P content from 1.0 to 7.0 wt % increased the H₂ production and COD removal from 6.43 to 8.34 mmol/g photocatalyst and from 26.0 to 50.6%, respectively. However, further increasing the P element content from 7.0 to 9.0 wt % diminished both the H₂ production and COD removal efficiency. This might be attributed to the combined effects of the altered surface charge (as the PZC value) and the reduced S BET of the Pₓ/TiO₂ photocatalysts. At low P element contents (1.0−7.0 wt %), increasing the P content decreased both the S BET and the PZC values of the respective Pₓ/TiO₂ photocatalysts (Table 1). The increased photocatalytic activity with the decreased S BET of the photocatalysts indicated the insignificant effect of the S BET on the photocatalytic activity. However, a low PZC value might induce high adjoining between PZC values and the pH of wastewater, which will promote contact or aggregation of the adjacent photocatalyst NPs in aqueous systems. The appropriate contact of solid NPs might in turn promote an effective transfer of e⁻ and h⁺ to the adjacent NPs under the employed thorough stirring condition, resulting in a prolonged e⁻−h⁺ lifetime as well as an enhanced photocatalytic activity of the Pₓ/TiO₂ photocatalysts. However, in the presence of a too high P element content (P > 7.0 wt %), the obtained Pₓ/TiO₂ photocatalyst exhibited an even lower S BET that could then restrict the amount of absorbed light. In addition, it displayed a low PZC value close to the pH of the wastewater, which would induce high contact or aggregation of adjacent photocatalyst NPs, forming a shading behavior and so limiting the capacity to absorb incident light. Consequently, the photocatalytic activity for H₂ production and COD removal was reduced.

2.4. Reusability of the Pₓ/TiO₂ Photocatalyst. The reusability of the Pₓ/TiO₂ photocatalyst was evaluated without any chemical or thermal treatment. After the first use, the photocatalyst NPs were separated from the processed wastewater by filtration and washed thoroughly with deionized water until the pH of the filtrate was close to that of deionized water. The ready-to-reuse Pₓ/TiO₂ photocatalyst was then obtained after drying at 105 °C for 3 h. The H₂ production and COD removal were found to decrease from 8.34 to 5.39 mmol/g photocatalyst and from 50.6 to 16.2%, respectively, from the first use to the fourth use (Figure 11). This decline was due to the loss of the P element from around 6.88 to 2.65% (figure not shown). Nevertheless, the photocatalytic activity of Pₓ/TiO₂ after the fourth use was still higher than that of the freshly calcined TiO₂.

The properties of the processed-biodiesel wastewater after photocatalysis using the Pₓ/TiO₂ catalyst (4.0 g catalyst/L loading and 5.93 mW/cm² for 4 h) are summarized in Table 2. It was clearly demonstrated that the quality of the biodiesel wastewater was improved by the photocatalytic process with Pₓ/TiO₂. Although the levels of some pollutants, measured in terms of the COD, oil and grease, and TDS levels, were still higher than the standard level set by the Thai Government for discharge into the environment, this work reclaims the use of a nonprecious photocatalyst to produce clean energy (H₂) by using an eco-friendly process.

Table 3 shows the comparative results of H₂ production and COD removal from biodiesel wastewater via commercial TiO₂ (P25) after being modified by heat treatment, metal decoration, heterojunctions with a semiconductor, and Nm doping (this work) at otherwise identical operating conditions (photocatalyst loading of 4.0 g/L and light intensity of 5.93 mW/cm² for 4 h). It clearly demonstrated that all the modified TiO₂ photocatalysts gave a higher H₂ production and
decreased H2 production and 68% reduced COD removal were obtained after the fourth use compared to the fresh P7/TiO2 wastewater due to its appropriate PZC value and pollutant removal than the calcined TiO2. Among all the modified TiO2 photocatalysts, the Pd-decorated TiO2 exhibited the highest H2 production level of up to 540 mmol at a loading of 4.0 g/L, a light intensity of 5.93 mW/cm2, and a radiation time of 4 h.

Table 2. Properties of the Fresh- and Processed-Biodiesel Wastewaters

| property                  | Thai standard | fresh wastewater | pretreated wastewatera | processed wastewaterb |
|---------------------------|---------------|------------------|-------------------------|-----------------------|
| pH                        | 5.5–9.0       | 4.61 ± 0.01      | 2.03 ± 0.02             | 2.21 ± 0.01           |
| soap (wt %)               |               | 2010 ± 11.0      | 1829 ± 10.0             | 1721 ± 4.25           |
| FFA (wt %)                | 1.50 ± 0.03   | 2.58 ± 0.08      | 1.13 ± 0.07             |                       |
| COD (mg/L)                | ≤400          | 15,083 ± 1060    | 7322 ± 736              | 3790 ± 494            |
| BOD (mg/L)                | ≤60           | 75.50 ± 1.50     | 15.0 ± 9.0              | 6.00 ± 1.06           |
| oil and grease (mg/L)     | ≤15           | 358.3 ± 25.0     | 163.1 ± 10.0            | 110.0 ± 36.7          |
| TDS (mg/L)                | ≤3000         | 1592 ± 15.0      | 2402 ± 11.7             | 2396.2 ± 3.9          |
| TS%                       | ≤150          | 308 ± 18.3       | 100 ± 13.3              | 55.0 ± 18.3           |

*a* Fresh-biodiesel wastewater was pretreated with concentrated H2SO4 to a pH of around 2. *b* Wastewater after photocatalytic processing using P7/TiO2 at a loading of 4.0 g/L, a light intensity of 5.93 mW/cm2, and a radiation time of 4 h.

3. CONCLUSIONS

In this work, the photocatalytic activity of the calcined TiO2 was improved by doping with C, Si, or P via ultrasonic-assisted impregnation. The P1/TiO2 photocatalyst exhibited the highest photocatalytic activity for H2 production and COD removal compared to the C1/TiO2, Si1/TiO2, and calcined TiO2 photocatalysts. This is because the doped P element furnished new optical properties to TiO2 by shortening the bandgap energy from 3.32 to 3.22 eV, so allowing more visible-light absorption. In addition, the positions of the VB and CB of P1/TiO2 still covered the potential to produce H2 and oxidizing agents in the system. In addition, it exhibited an appropriate surface charge, which can induce an effective transfer of \( e^- \) and \( h^+ \) as well as a prolongation of the \( e^-\text{−}h^+ \) lifetime. Varying the amount of the doped P element revealed that the P1/TiO2 gave the highest photocatalytic activity for simultaneous H2 production and COD removal from biodiesel wastewater due to its appropriate PZC value and \( \delta_{BET} \). A 35% decreased H2 production and 68% reduced COD removal were obtained after the fourth use compared to the fresh P1/TiO2 catalyst, but these values were still 1.5- and 2.0-fold higher, respectively, than those obtained with the pristine calcined TiO2.

4. MATERIALS AND METHODS

4.1. Preparation of the Nm/TiO2 Photocatalyst and Characterizations. The preparation of the Nm/TiO2 photocatalyst was adopted from the previous works. Three Nm elements (C, Si, and P) were individually doped into TiO2 by ultrasonic-assisted impregnation to form the Nm/TiO2 photocatalysts, where x is the content of Nm in the range of 1.0–9.0% by weight (wt %). Initially, TiO2 was prepared from the calcination of commercial TiO2 (P25; 99.5%, Sigma Aldrich) in a muffle furnace (PLF160/9B, Protherm) at 400 °C for 3 h.24 Next, approximately 2.97 g of calcined TiO2 was dispersed in 40 mL of 50% (v/v) ethanol (99.9%, Ajax) in distilled water. Meanwhile, approximately 0.0657 mL of phosphoric acid (85.0%, QRec) was mixed with 10 mL of distilled water by rigorous mixing for 15 min and then added into the above TiO2 slurry. The obtained acid slurry was stirred at 300 rpm for 1 h and successively sonicated in an ultrasonic bath (NXPC-2010(P)) for 30 min. The excess water was then eliminated from the solid substances via drying in an oven (BE-100) at 110 °C for 24 h. The remaining solid portion was ground using a ceramic mortar and subsequently calcined at 350 °C for 3 h, yielding a 1 wt % phosphorus-doped TiO2 (P1/TiO2) photocatalyst. A similar procedure was repeated to obtain a phosphorus content in the range of 3.0–9.0 wt %. For the C-doped TiO2 (C/TiO2) and Si-doped TiO2 (Si/TiO2), the same method was still used, except that glucose (99.5%, Ajax) and tetraethoxysilane (99.0%, Sigma Aldrich) were used as the C and Si precursors, respectively.

The point of zero charge (PZC) of all photocatalysts was measured via the pH drift method as previously reported. In brief, the initial pH value of the 0.1 M potassium nitrate (KNO3; Carlo Erba Reagent) solution was adjusted as required between pH 2 and 12 using either 0.1 M nitric acid (Qrec) or 0.1 M sodium hydroxide (Qrec). Then, approximately 0.4 g of the respective photocatalyst was dispersed in 20 mL of the respective pH-adjusted KNO3 solution. The obtained slurry was mechanically shaken at 120 rpm for 24 h. The aqueous solution was separated from the solid portion by filtration, and the final pH was measured using a pH meter (IQ150-77, IQ Scientific). The PZC value was estimated from the intersection point between the line curve of the initial versus final pH values and the line passing through the origin (initial pH = final pH).

The morphologies and optical properties of the prepared photocatalysts were examined as follows. The actual content of the Nm element doped on the TiO2 surface was examined via scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS; JEOL). The anatase content and crystal size of TiO2 in each prepared photocatalyst were calculated from the corresponding X-ray diffraction peaks obtained from the X-ray diffraction (XRD) analysis (D8 Advance, Bruker) using the Spurr and Myers and Debye and Scherrer equations, respectively. The bandgap energy was determined from the linear portion of the Tauc plot estimated from the UV−vis absorbance obtained using a UV−vis spectrophotometer (Lambda 950, PerkinElmer).

The textural properties of the prepared photocatalysts, including the surface area and pore size distribution, were examined via a surface area analyzer (Quantachrome, Autosorb-1) using the Brunauer−Emmett−Teller (BET) and BJH methods, respectively. The rate of \( e^-\text{−}h^+ \) recombination was qualitatively monitored using photoluminescence (PL) spectrometry (LS-55, PerkinElmer). The electron density state at the valence band (VB) of the Nm/TiO2 photocatalyst was...
evaluated using X-ray photoelectron spectroscopy (XPS; Axis Supra, Kratos).

4.2. Photocatalytic Activity of Nm\textsubscript{x}/TiO\textsubscript{2} Photocatalysts. The photocatalytic activity of each Nm\textsubscript{x}/TiO\textsubscript{2} photocatalyst was evaluated in terms of the simultaneous H\textsubscript{2} production and COD removal at room temperature (∼30 °C) and atmospheric pressure using industrial biodiesel wastewater (Table 2) as the feedstock (hydrogen source). Prior to performing each photocatalytic assay, the raw biodiesel wastewater, collected from a biodiesel production plant in Thailand that uses waste cooking oil as the raw material, was acidified to a pH of around 2\textsuperscript{,}6\textsuperscript{1} by the addition of concentrated sulfuric acid (98%, QRec).

The initial properties of the raw and acid-treated wastewater were analyzed as follows. The pH was measured using a pH meter (IQ150−77), while the levels of COD, biological oxygen demand (BOD), oil and grease, total dissolved solids (TDS), and total suspended solids (TSS) were measured according to standard methods\textsuperscript{65} and the soap and free fatty acid (FFA) contents by potentiometric titration with 0.01 M hydrochloric acid and 0.1 M potassium hydroxide, respectively.\textsuperscript{66,67} Next, 100 mL of either pretreated or diluted pretreated wastewater plus 0.4 g of the respective photocatalyst was placed in a cylindrical glass reactor, located centrally in a UV-protected box equipped with a 120 W high-pressure mercury lamp (100–600 nm, RUV533 BC) on the top. Argon (Ar; 99.999%, Linde) was supplied to the photoreactor at a flow rate of 500 mL/min to sweep air from the reactor. At the same time, the liquid slurry was stirred thoroughly at 400 rpm for 1 h to allow the equilibrium adsorption of pollutants on the surface of photocatalysts. The Ar supply was then terminated, and both the inlet and outlet gas valves were closed to initiate a closed system with an inert environment. The photoreactor was then irradiated via the UV lamp at a constant light intensity of 5.93 mW/cm\textsuperscript{2} for 4 h. Throughout the experiment, the temperature of the photoreactor was maintained at 30 °C using an automatic temperature controller (HS-28A). When the experiment was finished, the generated gas was harvested from the reactor using Ar as the carrier gas and analyzed for its composition and concentration using gas chromatography (Shimadzu 2014) with a thermal conductivity detector. The processed wastewater in the presence of the solid catalysts was filtered in the filtration unit using an electrical pump (66688, Suoka) to separate the filtrate from the solid portion, and then, the properties of the processed wastewater were analyzed.

Table 3. H\textsubscript{2} Production and COD Removal from Biodiesel Wastewater via a Photocatalytic Reaction at Otherwise Identical Operating Conditions (Photocatalyst Loading of 4.0 g/L, Light Intensity of 5.93 mW/cm\textsuperscript{2}, and Irradiation Time of 4 h)

| Photocatalyst | H\textsubscript{2} production (mmol) | COD (mg/L) | Oil and grease (mg/L) | Soap (mg/L) | FFA (mg/L) |
|---------------|----------------------------------|------------|----------------------|-------------|------------|
| Nm\textsubscript{40}/TiO\textsubscript{2} | 26.00 ± 14.1 | 247.34 | 0.002 ± 0.04 | 0.09 ± 0.09 | 2.21 ± 0.01 |
| Nm\textsubscript{540}/TiO\textsubscript{2} | 11.0 ± 0.09 | 196.85 ± 4189 | 2.21 ± 0.01 | 2.21 ± 0.01 | 2.21 ± 0.01 |
| Nm\textsubscript{3.79}/TiO\textsubscript{2} | 187 ± 10.0 | 270.08 ± 1016 | 187 ± 10.0 | 187 ± 10.0 | 187 ± 10.0 |
| Nm\textsubscript{3.34}/TiO\textsubscript{2} | 3.79 | 18.9 ± 0.50 | 3.79 | 3.79 | 3.79 |

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Notes

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