Core/Shell Nitrogen-Doped TiO$_2$@SiO$_2$ Nano-Catalyst as an Additive in Photocatalytic Paint for Gaseous Acetaldehyde Decomposition

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Abstract: A nitrogen-doped TiO$_2$@SiO$_2$ core/shell nano-photocatalyst (N-TiO$_2$@SiO$_2$) was used as an additive in photocatalytic paint and applied for the photocatalytic degradation of gaseous acetaldehyde under light-emitting diode (LED) visible light irradiation. N-TiO$_2$ was synthesised via the solvothermal method and then encapsulated by SiO$_2$ via the sol-gel method. The incorporation of the N atom into the TiO$_2$ structure was observed by X-ray photoelectron spectroscopy. The N-TiO$_2$@SiO$_2$ core/shell structure was determined by TEM images. The photodegradation of gaseous acetaldehyde using the prepared N-TiO$_2$@SiO$_2$ photocatalytic paint was examined in a closed chamber under LED light irradiation. The photodegradation of acetaldehyde by N-TiO$_2$@SiO$_2$ photocatalytic paint (31%) was significantly higher than that of TiO$_2$ paint (5%) and N-TiO$_2$ paint (20%) within 16 h. The chemical resistance and adhesion ability of N-TiO$_2$@SiO$_2$ photocatalytic paint were investigated following Thai Industrial Standards (TIS) no. 2321 and standard test methods for rating adhesion by tape test (ASTM D 3359-22). The N-TiO$_2$@SiO$_2$ paint showed good acid and alkali resistance, as well as high adhesion ability comparable with commercial paint (without a photocatalyst).

Keywords: N-doped titanium dioxide; silica; photocatalytic paint; core/shell photocatalyst; acetaldehyde

1. Introduction

Today, indoor air quality (IAQ) has become a significant public concern. Most people spend 80–90% of their time living indoors such as in households, vehicles, shopping centres, and offices [1–4]. The significant parameters that affect IAQ include the construction materials and furniture in households, as well as the human activities in buildings [5,6]. Indoor air pollution (IAP) includes NO$_x$, volatile and semi-volatile organic compounds (VOCs), SO$_2$, O$_3$, CO, PM, radon, toxic metals, and microorganisms. The sources of VOCs are mostly generated from human activities indoors, such as cooking, solvent use, cleaning reagent use, tobacco smoke, etc. [7,8]. Due to their low boiling point, they are easily volatile at room temperature and accumulate in indoor environments. Short-term exposure to VOCs can cause adverse effects on human health, including headache and nausea as well as eye, nose, and throat irritation. These symptoms are commonly attributed to sick-building syndrome (SBS) [9]. Chronic exposure to VOCs can lead to serious health problems, such as failure of the liver and kidneys, respiratory diseases, and cancer [10]. The common VOCs found in indoor air include benzene, toluene, formaldehyde, acetaldehyde, etc. Acetaldehyde is a major compound in tobacco smoke [11–13]. The United States Environmental Protection
Agency discovered that tobacco smoke accumulated more indoors than it did outside \[14\], indicating that people are subjected to a higher risk of exposure to acetaldehyde indoors than they would be outside. Thus, acetaldehyde is one of the most significant VOCs in households and office buildings.

Various VOCs treatments have been studied, such as filtration \[15\], adsorption \[16\], ozonation \[17\], and photocatalysis \[18\]. Among these treatment methods, the photocatalytic reaction is one of the most promising applications for VOC purification. Photocatalysis is the acceleration of a photo-induced reaction by a catalyst. Photocatalytic processes have four steps, including (i) stimulation of the photocatalyst by light adsorption, (ii) generation of the electron (\(e^-\)) and hole (\(h^+\)) in the valence band (VB) and conduction band (CB), (iii) the electron (\(e^-\)) reacts with oxygen (\(O_2\)) while the hole (\(h^+\)) reacts with water (\(H_2O\)) and produces superoxide radicals (\(O_2^-\)) and hydroxyl radicals (\(OH^*\)), respectively, and (vi) both \(O_2^-\) and \(OH^*\) oxidise and reduce the pollutants \[19,20\]. Titanium dioxide (\(TiO_2\)) is a common photocatalyst widely used for photocatalytic applications \[21\]. It possesses many advantages compared with other photocatalysts, such as low cost \[22\], good stability \[23\], and environmental responsiveness \[24\]. Many studies have focused on using \(TiO_2\) as an additive in surface coating applications. Islam et al., (2020) \[25\] developed photocatalytic paint based on \(TiO_2\) nanoparticles and acrylate-based photopolymer resin. They found that the \(TiO_2\) embedded in the polymer could generate \(OH^*\) under UV-B light and sunlight, enabling 80–90% photocatalytic degradation of methylene blue (MB) and methyl orange (MO) under sunlight and UV-B light. Basso et al., (2020) \[26\] produced photocatalytic paint by adding \(TiO_2\) P25 powder to an acrylic-based paint. The photocatalytic paint could reduce toluene with a photocatalytic efficiency of 15% under UV light. At present, \(TiO_2\) is commercially used in photocatalytic paints to provide a self-cleaning function. However, it is known that \(TiO_2\) photocatalytic paint involves drawbacks, including (1) limited photocatalytic performance of \(TiO_2\) under visible light irradiation in an indoor environment and (2) self-degradation when adding bare \(TiO_2\) to acrylic paint due to degradation of the organic binder in the paint.

An alternate approach to enhance the photocatalytic performance of \(TiO_2\) under visible light irradiation is nitrogen doping. Meroni et al., (2011) \[27\] modified \(TiO_2\) with nitrogen (N-doped \(TiO_2\)) by the sol-gel method. They found that the energy band gap of N-doped \(TiO_2\) was narrower than that of pure \(TiO_2\) due to N species being substitutional and interstitial in the \(TiO_2\) anatase structure. The photodegradation of ethanol and acetaldehyde using N-doped \(TiO_2\) under UV and solar irradiation was then examined. The reaction rate of ethanol and acetaldehyde degradation under UV and solar irradiation by N-doped \(TiO_2\) was higher than that of pure \(TiO_2\). He et al., (2013) \[28\] studied benzene degradation under UV irradiation using N-doped \(TiO_2\) synthesised via the solvothermal method. The results showed that the N-doped \(TiO_2\) achieved the highest photocatalytic degradation and remained unchanged after being recycled 15 times. After doping, the particle sizes of N-doped \(TiO_2\) significantly decreased and the specific surface area of N-doped \(TiO_2\) significantly increased. Sirivallop et al., (2020) \[29\] synthesised N-doped \(TiO_2\) using the solvothermal method applied for the degradation of MB and ammonia (\(NH_3\)) under LED irradiation. The N-doped \(TiO_2\) provided a narrowing energy band gap, and the photodegradation performance of MB and \(NH_3\) under LED irradiation using N-doped \(TiO_2\) was significantly higher than that of pure \(TiO_2\). It was also found that N-doped \(TiO_2\) had a pale yellow colour. Thus, it could be added to paint without changing the colour tone.

Regarding self-degradation in the paint caused by photocatalysts, encapsulating the highly reactive \(TiO_2\) photocatalyst is recommended. The core/shell technique is a new alternative approach to encapsulating \(TiO_2\) inside inert compounds. With this method, the specific surface area is significantly improved because the core/shell structure can enhance particle distribution and prevent particle agglomerations, which are the key factors in the enhancement of photocatalytic activity \[30,31\]. Silicon dioxide (\(SiO_2\)) is mostly used as a shell due to its unique properties, such as thermal and chemical stability, easy reuse, and
enhanced light transmission with minimum reflection [32]. The advantages of SiO\textsubscript{2} used as a shell in TiO\textsubscript{2}@SiO\textsubscript{2} nano-catalyst were increasing specific surface area, protecting TiO\textsubscript{2} aggregation, preventing charge recombination, and providing acid sites on the surface, which could enhance the adsorption capacity and photocatalytic performance of the photocatalytic paint [33]. Mahanta et al., (2022) [34] synthesised TiO\textsubscript{2}@SiO\textsubscript{2} photocatalysts by the sol-gel method. The photocatalysts had high crystallinity and a large specific surface area. The TiO\textsubscript{2}@SiO\textsubscript{2} photocatalyst was then applied to decolourise methylene blue (MB) under sunlight and UV light. The decolourisation efficiency of MB under sunlight and UV light using TiO\textsubscript{2}@SiO\textsubscript{2} was approximately 90% and 85%, respectively. Wang et al., (2020) [35] synthesised TiO\textsubscript{2}@SiO\textsubscript{2} photocatalyst and coated it on a cement substrate for the decomposition of pollutants in outdoor environments. The photocatalytic performance of TiO\textsubscript{2}@SiO\textsubscript{2} coated on cement was evaluated by the decolourisation of rhodamine B (RhB) under UV light irradiation. The results found that the SiO\textsubscript{2} coated on the TiO\textsubscript{2} surface had a large specific surface area. The RhB photodegradation efficiency using TiO\textsubscript{2}@SiO\textsubscript{2} coated on cement was approximately 73%, which was higher than that of TiO\textsubscript{2} P25 coated on cement (60%).

This research aims to develop visible-light responsive photocatalytic paint using an N-doped TiO\textsubscript{2}-SiO\textsubscript{2} core/shell nano-catalyst (TiO\textsubscript{2}@SiO\textsubscript{2}) as an additive in emulsion-based paint. N-doped TiO\textsubscript{2} was synthesised by the solvothermal method and then encapsulated with SiO\textsubscript{2} by the sol-gel method. The physical and chemical properties of the photocatalytic paint were tested following Thai Industrial Standards (TIS) and the American Society for Testing and Materials (ASTM). The performance of the photocatalytic paint for the degradation of gaseous acetaldehyde was examined under LED visible light irradiation in a closed chamber.

2. Results and Discussion

2.1. Nano-Photocatalyst Characteristics

2.1.1. Crystalline Structure

The crystalline structures of SiO\textsubscript{2}, TiO\textsubscript{2}, N-TiO\textsubscript{2}, and N-TiO\textsubscript{2}@SiO\textsubscript{2} core/shell were determined by the XRD technique (Figure 1). The XRD patterns were identified by Joint Committee on Powder Diffraction Standard. The board XRD peak at 23.5° was observed on the SiO\textsubscript{2} sample, corresponding to standard amorphous silica (JCPDS No. 29-0085), while the diffraction peaks of TiO\textsubscript{2}, N-TiO\textsubscript{2}, and N-TiO\textsubscript{2}@SiO\textsubscript{2} core/shell were similar. The peaks that appeared at 25.3°, 37.8°, and 48.2° were referred to as standard TiO\textsubscript{2} anatase (JCPDS No. 21-1272), at (101), (004), and (200) planes, respectively. No evident peak referring to nitrogen was observed due to low nitrogen content in the N-doped samples, nor could the diffraction peak of SiO\textsubscript{2} be observed. This might have been caused by well-dispersed silica on the surface of the N-TiO\textsubscript{2} photocatalyst.

2.1.2. Surface Morphology

The surface morphology of TiO\textsubscript{2}, N-TiO\textsubscript{2}, and N-TiO\textsubscript{2}@SiO\textsubscript{2} core/shell was examined using TEM images, as shown in Figure 2. The TEM photograph demonstrates the aggregation of TiO\textsubscript{2} (Figure 2a) and N-TiO\textsubscript{2} particles (Figure 2b), while Figure 2c exhibits the core/shell structure of the N-TiO\textsubscript{2}@SiO\textsubscript{2} nano-photocatalyst. The SiO\textsubscript{2} shells (thin transparent layers) are uniformly deposited on the N-TiO\textsubscript{2} cores (black spots), resulting in better particle dispersion than that of the N-TiO\textsubscript{2} particles. The SiO\textsubscript{2} shell thickness of the N-TiO\textsubscript{2}@SiO\textsubscript{2} core/shell was approximately 20–30 nm. The particle size distribution (see Figure S1 in Supplementary Material) was determined based on the SEM images (see Figure S2 in Supplementary Material). The results showed that the mean particle sizes of TiO\textsubscript{2}, N-TiO\textsubscript{2}, and N-TiO\textsubscript{2}@SiO\textsubscript{2} core/shell were approximately 15–25 nm, 16–22 nm, and 30–40 nm, respectively.
2.1.3. Chemical Composition

The EDX spectra were used to indicate the existence of N, Si, and Ti elements in the N-TiO$_2$@SiO$_2$ core/shell compared with the N-TiO$_2$ nano-catalyst, as shown in Figure S3 in Supplementary Material. Furthermore, the XPS analysis (see Figure 3) was used to investigate elemental composition as well as the chemical and electronic states of the elements in the nano-catalysts.

The XPS spectra of TiO$_2$, N-TiO$_2$, and N-TiO$_2$@SiO$_2$ core/shell, presented in Figure 3a, indicated the Ti 2p peak binding energies for Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ [36]. The peaks of Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ of TiO$_2$ were 465 and 459 eV, respectively. It was observed that the Ti 2p$_{1/2}$ peak of N-TiO$_2$ was shifted to a lower binding energy than that of TiO$_2$. Similarly, the Ti 2p$_{1/2}$ peak of N-TiO$_2$@SiO$_2$ core/shell was slightly shifted to a lower binding energy than that of N-TiO$_2$. The shifts in Ti 2p$_{1/2}$ spectra were due to the incorporation of N and Si atoms into the TiO$_2$ structure. The O 1S spectra of all samples, shown in Figure 3b, indicated the Ti-O-Ti bonding (530 eV) in TiO$_2$, N-TiO$_2$, and N-TiO$_2$@SiO$_2$ core/shell. In addition, the binding energy of the O 1s peak that indicated the interaction between the SiO$_2$ shell and N-TiO$_2$ core of the N-TiO$_2$@SiO$_2$ nano-catalyst was observed at 532 eV (Ti–O–Si)$_8$, corresponding with the blue shift of the binding energy of the Ti 2p$_{3/2}$ peak for N-TiO$_2$@SiO$_2$ core/shell [37,38]. The N 1s spectra of N-TiO$_2$ and N-TiO$_2$@SiO$_2$ core/shell also recognised three peaks, corresponding to N–O (403 eV), Ti–O–N (400 eV), and Ti–N–Ti (398 eV) bonding, respectively (Figure 3c). The N–O bonding related to the signal...
of nitrogen species [39], while the Ti–O–N and Ti–N–Ti were attributed to the nitrogen interstitial and substitutional incorporation into the TiO$_2$ lattice, respectively [40,41]. The Si 2p spectrum of N-TiO$_2$@SiO$_2$ core/shell displayed in Figure 3d indicated a peak at about 103.36 eV, which was attributed to Si–O–Si [42]. The TEM images and XPS results confirmed the existence of the SiO$_2$ shell coated on the N-TiO$_2$ core and indicated the interaction between N, Si, and TiO$_2$ in the N-TiO$_2$@SiO$_2$ core/shell nano-catalyst.

![Figure 3. The XPS spectra of TiO$_2$, N-TiO$_2$, and N-TiO$_2$@SiO$_2$ core/shell for (a) Ti 2p, (b) O 1s, (c) N 1s, and (d) Si 2p.](image)

### 2.1.4. Specific Surface Area and Porosity

N$_2$ adsorption-desorption isotherms and pore size distributions of TiO$_2$, N-TiO$_2$, and N-TiO$_2$@SiO$_2$ core/shell were measured by the BET method, as shown in Figure 4. All isotherms were classified as type IV in the IUPAC classification, referring to mesoporous material [43]. The isotherms of TiO$_2$ and N-TiO$_2$ had an H2a hysteresis loop, indicating the narrow pore diameter and complicated pore shape of mesoporous, whereas the core/shell N-TiO$_2$@SiO$_2$ isotherm displayed an H2b hysteresis loop, indicating a characteristic of mesoporous silica [44]. The pore size distributions of TiO$_2$, N-TiO$_2$, and N-TiO$_2$@SiO$_2$ core/shell were narrow, and the average pore diameters were in a range between 5–25 nm. According to BET analysis, the specific surface area of the N-TiO$_2$ nano-catalyst was increased from 40 m$^2$g$^{-1}$ to 157 m$^2$g$^{-1}$ after incorporating the SiO$_2$ shell. This result was in agreement with Mahanta et al., (2022) [34]. The large specific surface area could
promote the adsorbability and photocatalytic activity of the nano-catalyst, which would help improve the photocatalytic degradation of organic pollutants [45,46].

![N2 adsorption-desorption isotherms](a)

![N2 adsorption-desorption isotherms](b)

![N2 adsorption-desorption isotherms](c)

![N2 adsorption-desorption isotherms](d)

**Figure 4.** N$_2$ adsorption-desorption isotherms of (a) TiO$_2$, (b) N-TiO$_2$, (c) N-TiO$_2$@SiO$_2$ core/shell, and (d) pore size distribution.

2.1.5. Absorption Edge and Band Gap Energy

Figure 5 shows the UV-Vis-NIR spectra and Tauc plots (inset) of N-TiO$_2$ and N-TiO$_2$@SiO$_2$ core/shell, observed in the wavelength range of 200–700 nm. The absorption edge of the TiO$_2$@SiO$_2$ core/shell shifted to a lower wavelength than that of N-TiO$_2$, indicating the blue shift effect (increasing bandgap energy). The bandgap energy calculated by the Tauc plot of TiO$_2$@SiO$_2$ core/shell was 2.92 eV, while the bandgap energy of N-TiO$_2$ was 2.79 eV. The blue shift effect of the SiO$_2$ shell-coated N-TiO$_2$ core was caused by two mechanisms. Firstly, the addition of SiO$_2$ considerably reduced the particle size of the N-TiO$_2$@SiO$_2$, leading to the quantum size effect (from bulk to nanoparticles). Secondly, the change in the electronic structure of Ti-O-Si bonds found in the N-TiO$_2$@SiO$_2$ core/shell required higher energy for electrons moving from the valence band to the conduction band [47].
2.2. Photocatalytic Paint

2.2.1. Acid and Alkali Resistance

The results of acid and alkali resistance of the commercial paint (without photocatalyst), TiO\textsubscript{2}, N-TiO\textsubscript{2}, and N-TiO\textsubscript{2}@SiO\textsubscript{2} photocatalytic paints are illustrated in Figures 6 and 7. After the samples were swamped in the acid and alkali solution for 18 h at room temperature, the swelling of the TiO\textsubscript{2} paint film and the crack of the N-TiO\textsubscript{2} paint film were observed, indicating no resistance to the acid and alkali solution. While no change on the film surface was observed on the samples coated by commercial and N-TiO\textsubscript{2}@SiO\textsubscript{2} paints. Self-degradation in the paint can occur when the photocatalyst is exposed to light and water in the environment. The photocatalyst produces hydroxyl radicals and superoxides, which can degrade the organic compounds in the paint, resulting in self-degradation. The results infer that the TiO\textsubscript{2}@SiO\textsubscript{2} core/shell structure provides an advantage in film protection. Without a SiO\textsubscript{2} shell, the photocatalyst could degrade organic binders. Furthermore, severe degradation was seen when the films were exposed to an acid and alkali solution, especially for the N-TiO\textsubscript{2} paint film.

![Figure 5. UV-Vis Near-Infrared spectrum and band gap energy calculated by Tauc plot (inset) of TiO\textsubscript{2}, N-TiO\textsubscript{2}, and core/shell N-TiO\textsubscript{2}@SiO\textsubscript{2}.](image)

![Figure 6. The acid resistance tests of commercial paint (without photocatalyst), TiO\textsubscript{2} paint, N-TiO\textsubscript{2} paint, and N-TiO\textsubscript{2}@SiO\textsubscript{2} paint.](image)
2.2.2. Adhesion Test

The results of the cross-cut test are presented in Figure 8. The adhesion performance can be classified into six levels, including (5B) not removed, (4B) less than 5%, (3B) about 5–15%, (2B) 15–35%, (1B) 35–65%, and (0B) greater than 65%. The adhesion performances of all films were ranked from the highest to the lowest adhesion ability as follows: Commercial emulsion paint (5B), N-TiO$_2$@SiO$_2$ paint (4B), TiO$_2$ paint (3B), and N-TiO$_2$ paint (0B), respectively. The trend was similar to the results of acid and alkali resistance. The N-TiO$_2$ paint exhibited the worst performance because the photocatalytic reactivity of TiO$_2$ was enhanced by N doping. Due to the high photocatalytic reactivity of the N-TiO$_2$ photocatalyst, the organic binder tended to be easily degraded. Incorporating SiO$_2$ as a core in N-TiO$_2$ could significantly improve the chemical resistance and adhesion ability of the paint film. Similar to other studies, it was reported that the important role of the SiO$_2$ shell was preventing self-degradation in paint [35,48,49]. Since the acid and alkali resistance and adhesion performance of TiO$_2$@SiO$_2$ paint were comparable with commercial paint, the N-TiO$_2$@SiO$_2$ paint was proposed as a promising photocatalytic paint, especially for indoor applications.

2.2.3. Photocatalytic Decomposition of Gaseous Acetaldehyde

Figure 9 shows the acetaldehyde removal in the dark and under LED irradiation. In the dark, the adsorption capacity of N-TiO$_2$@SiO$_2$ paint (10.31%) was the highest, followed by N-TiO$_2$ paint (5.62%), TiO$_2$ paint (4.30%), and commercial paint (<1%), respectively. Similar to the adsorption in the dark, the N-TiO$_2$@SiO$_2$ paint exhibited the highest acetaldehyde degradation efficiency under LED irradiation (31.49%) compared with N-TiO$_2$ paint (17.71%) and TiO$_2$ paint (5.01%). It was clear that nitrogen doping on TiO$_2$ could significantly enhance the photocatalytic reactivity of TiO$_2$ under LED irradiation. When the nitrogen atom was doped into the TiO$_2$ structure, the new mid-band gap above the valence band of TiO$_2$ was created. This narrowed bandgap could facilitate the movement of electrons in the valence band to the conduction band under LED irradiation. Moreover, it was noted that incorporating a SiO$_2$ shell into TiO$_2$ could improve both the adsorption
capacity and photocatalytic reactivity of the photocatalyst. The impressive performance of N-TiO$_2$@SiO$_2$ paint was mainly contributed by the SiO$_2$ shell. The encapsulation of N-TiO$_2$ with a SiO$_2$ shell could increase the specific surface area of the catalyst and reduce particle aggregation. These advantages also help improve particle dispersion in the paint. Moreover, the SiO$_2$ shell could provide more reactive acid sites (silanol groups) and prevent charge recombination in photocatalysis.

![Graph showing photocatalytic performance](image)

**Figure 9.** Adsorption (in the dark) and photocatalytic performance of gaseous acetaldehyde decomposition by different photocatalytic paints under LED visible light at room temperature within 16 h.

The comparison between the photocatalytic performance of N-TiO$_2$@SiO$_2$ paint in this study and other similar studies can be described as follows. Islam et al., (2020) [25] developed a photocatalytic paint based on TiO$_2$ and photopolymer resin. The photocatalytic performance of the paint was examined by photodegradation of MO and MB dye in water under UV-B and sunlight irradiation. This study found that the highest photodegradation efficiency of MO and MB dye in water under sunlight irradiation was approximately 90% in 60 min. Unlike the current study, the photocatalytic paint prepared by Islam et al., (2020) used a photopolymer resin as a binder, not a commercial emulsion paint. Moreover, the photocatalytic performance was tested under UV rather than visible light irradiation. This photocatalytic paint might be suitable for external uses. Basso et al., (2018) [26] used TiO$_2$ P25 powder as an additive in acrylic-based paint for toluene degradation. The photodegradation performance of toluene under UV-A irradiation was approximately 32.6% for 10 min. The results indicated the toluene degradation and the self-degradation of organic compounds in the paint composition; the N-TiO$_2$@SiO$_2$ photocatalytic paint prepared in this study could degrade acetaldehyde even under visible light irradiation without degrading an organic binder. Accordingly, the N-TiO$_2$@SiO$_2$ photocatalytic paint in this study is a promising material for commercial interior paint.

Apart from nitrogen dopant, Ag dopant is a promising metal used to improve the photocatalytic performance of TiO$_2$. Kumar et al., (2016) [50] studied Ag nanoparticle decorated TiO$_2$ nanorod array (Ag-TiO$_2$) substrates using a glancing angle deposition (GLAD) technique for photocatalysis and surface-enhanced Raman scattering (SERS) applications. The photocatalytic performance of the Ag-TiO$_2$ was evaluated by the degradation of rhodamine 6G (Rh6G) under UV irradiation. They reported that the Ag-TiO$_2$ could degrade 90% of Rh6G under UV irradiation within 90 min. Singh et al., (2018) [51] synthesised Ag-TiO$_2$ hybrid nanoparticles by CTAB-assisted wet chemical synthesis and applied the photocatalysts for the photocatalytic degradation of MB dye under solar light irradiation.
The results showed that the hybrid material could remove 89.2% of MB dye under solar light irradiation within 60 min, higher than bare TiO$_2$ (50.1%). Even though the Ag dopant could improve the photocatalytic reactivity of TiO$_2$, Ag played a different role when compared with N dopant. The N dopant helped uplift the valence band towards the conduction band [52], while the Ag dopant helped extend light absorption toward a visible region by surface plasmon resonance, as well as delay the recombination rate of electrons and holes of TiO$_2$ [29]. The pale yellow N-doped TiO$_2$ particles also had an advantage over the grey Ag-TiO$_2$ particles. The N-doped TiO$_2$ particles could be added without affecting the colour shade of the paint.

The kinetic reaction of photocatalytic degradation of acetaldehyde was studied using Equation (1)

$$\ln \left( \frac{C_0}{C} \right) = kt$$

where $C_0$ is the initial concentration of acetaldehyde (50 ppm), $C$ is the concentration of acetaldehyde (ppm) after time (t), and $k$ is the pseudo-first-order rate (h$^{-1}$). The photocatalytic degradation of acetaldehyde fits with a pseudo-first-order model, as shown in Figure 10. The calculated pseudo-first-order kinetic constants ($k$) of TiO$_2$ paint, N-TiO$_2$ paint, and N-TiO$_2$@SiO$_2$ paint were 0.0062 h$^{-1}$, 0.0228 h$^{-1}$, and 0.0455 h$^{-1}$, respectively. The reaction constant of N-TiO$_2$@SiO$_2$ paint was the highest and nearly two times higher than that of N-TiO$_2$ paint.

Figure 10. Pseudo-first-order models of gaseous acetaldehyde photodegradation by different photocatalytic paints under LED visible light at room temperature within 6 h.

Figure 11 illustrates the hypothesised mechanism of acetaldehyde photocatalytic degradation using N-TiO$_2$@SiO$_2$ paint. The N doping on the TiO$_2$ structure creates a new mid-band gap above the valence band (VB) of TiO$_2$. The LED light energises electrons in the VB, and then the excited electrons move to the conduction band (CB), leaving the hole ($h^+$) in the VB. The SiO$_2$ shell coated on the N-TiO$_2$ core helps increase the adsorption of the acetaldehyde molecules on the film surface. The excited electrons in the VB react with oxygen ($O_2$) in the air, generating superoxide radicals ($O_2^-$), while the H$_2$O molecules adsorbed by $h^+$ in the CB produce hydroxyl radicals (OH$^*$). Both active radicals decompose the gaseous acetaldehyde molecules into various small molecules and, finally, into CO$_2$ and H$_2$O. The hypothesised decomposition mechanism is described in Equation (2) [53].

$$\begin{align*}
\text{CH}_3\text{CHO} + \text{OH}^* & \rightarrow \text{CH}_3\text{COOH} \\
\text{CH}_3\text{COOH} + \text{OH}^* & \rightarrow \text{CH}_3\text{COOH} \\
\text{CH}_2\text{O} + \text{OH}^* & \rightarrow \text{H}_2\text{O} \\
\text{CH}_2\text{O}_2 + \text{OH}^* & \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}$$
3. Materials and Methods

3.1. Materials

Titanium (IV) butoxide (TBOT, 97%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethanol (99.8%), Nitric acid (HNO₃), and Hydrochloric acid (HCl, 37%) were purchased from Qrec (New Zealand). Diethylene-amine (DEA, 99%), Tetraethyl orthosilicate (TEOS, 99.99%), Methylene blue (MB) (C₆H₁₈N₃CIS.2H₂O, ≥ 96%), and Acetaldehyde (CH₃CHO, ≥ 99.5%) were purchased from Merck (Rahway, NJ, USA). These chemicals were used for the synthesis of the core/shell nano-photocatalyst.

Ammonia (NH₃, 25%) was purchased from Qrec, New Zealand. Polycarboxylic acid sodium salt (CARRYBON L-400) used as a dispersing agent was purchased from Sanyo Kasei Ltd. (Bankhai, RYG, Thailand), ULTRABOND P261 acrylic, Hydroxyethyl cellulose (cellosize), and water treatment defoamer (E-193) were purchased from Chemical Village Co., Ltd. (Bangplee, SPK, Thailand). These chemicals were used to prepare the photocatalytic paint. Finally, calcium hydroxide (Ca(OH)₂) was purchased from Merck (Rahway, NJ, USA) and used for the alkali resistance test.

3.2. Nano-Photocatalyst Preparations

TiO₂ and N-doped TiO₂ photocatalysts were synthesised by the solvothermal method, and then N-doped TiO₂@SiO₂ core/shell photocatalysts were synthesised by the sol-gel method, following [33,54]. The molar ratios of the synthesised photocatalysts were 1Ti(OC₄H₉)₄:18C₂H₅OH:2H₂O:0.2HNO₃. TBOT was dissolved in ethanol and then the nitric solution was added to the TBOT solution. The solution was stirred at room temperature for 2 h and then transferred into a Teflon-lined stainless-steel autoclave. The autoclave was placed in an oven and heated to 150 °C for 5 h. After that, the suspended solid was separated by a centrifuge and washed with DI water and ethanol before being calcined at 450 °C for 3 h. The obtained white powder was TiO₂ photocatalyst. To prepare an N-doped TiO₂ (named N-TiO₂) photocatalyst, 5% mol of DEA in ethanol was added to the TBOT solution before being transferred to an autoclave.

The synthesis of the N-doped TiO₂@SiO₂ core/shell nano-photocatalyst (N-TiO₂@SiO₂) was modified from [33,54]. TEOS, as a SiO₂ precursor, was dissolved in 50 mL of ethanol solution, and then the N-TiO₂ photocatalyst was added into the TEOS solution (molar ratio of Ti:Si = 1:1.5). The pH of the mixture was then adjusted to 10 by adding 1 M of HCl. The solution was constantly stirred at 80 °C for 17 h to complete the synthesis reaction. The suspended solid was then precipitated using a centrifuge, washed with DI water, and calcined at 550 °C for 2 h. The final product was the N-TiO₂@SiO₂ core/shell nano-photocatalyst.
3.3. Nano-Photocatalyst Characterizations

The crystal structures of all nano-photocatalysts were investigated by an X-ray diffractometer (XRD, D8 Advance with Eulerian Cradle, Bruker, Billerica, MA, USA) with Cu Kα radiation (λ = 1.54 Å). The morphology was observed via Field Transmission Electron Microscopy (FE-TEM, JEM-3100F, Tokyo, Japan). The specific surface area was determined from the Brunauer-Emmett-Teller (BET) method by N₂ gas adsorption-desorption isotherms at 77 K with a surface analyser (Autosorb-1, Quantachrome, BEL model, Waltham, MA, USA). The pore size distribution was evaluated from the N₂ desorption by the Barrett-Joyner-Halenda (BJH) method. The elemental composition was obtained using energy dispersive X-ray spectroscopy (EDX, Oxford, INCAx-act, Tokyo, Japan) and X-ray photoelectron spectroscopy (XPS). The absorption edge was analysed by an Ultraviolet-Visible-Near Infrared (UV-VIS-NIR, Perkin Elmer, Lambda 950, Waltham, MA, USA) spectrometer within the range of 300–800 nm.

3.4. Photocatalytic Paint Preparation

Photocatalytic paint, with and without photocatalysts, was prepared using the following commercial formula, as shown in Table 1. Bare TiO₂, N-TiO₂, and N-TiO₂@SiO₂ core/shell nano-photocatalysts were used as paint additives. The procedure for the photocatalytic paint preparation is illustrated in Figure 12. The nano-photocatalyst powder was dispersed in DI water by homogeniser at 4000 rpm for 30 min. CARRYBON L-400, E-193, and cellosize were added to the nano-photocatalyst solution. After that, the slurry mixture was stirred by a homogeniser at 4000 rpm for 45 min. Then, NH₃, E-193, and acrylic P261 were added to the slurry mixture and stirred by a homogeniser at 6000 rpm for 1 h. The final products were photocatalytic paints.

Table 1. Formulation of the photocatalytic paint.

<table>
<thead>
<tr>
<th>Ingredient of Photocatalytic Paint</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano-photocatalyst powder</td>
<td>3.60</td>
</tr>
<tr>
<td>DI water</td>
<td>72.53</td>
</tr>
<tr>
<td>Dispersing agent (CARRYBON L-400)</td>
<td>0.36</td>
</tr>
<tr>
<td>Defoamer (E-193)</td>
<td>0.54</td>
</tr>
<tr>
<td>Cellosize</td>
<td>1.08</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.18</td>
</tr>
<tr>
<td>Acrylic (P261)</td>
<td>21.71</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

3.5. Standard Testing of the Photocatalytic Paints

The acid and base resistance of the prepared photocatalytic paint was tested following the Thai Industrial Standards (TIS) no. 2321, while the adhesion performance of the paint film was evaluated following International Standards no. ASTM D 3359-22 (Standard Test Methods for Rating Adhesion by Tape Test). Square concrete samples 3 cm × 3 cm in size were coated with the photocatalytic paints (TiO₂, N-TiO₂, and N-TiO₂@SiO₂) and commercial emulsion paint (without photocatalyst), and then dried at room temperature for 2 days. For the acid resistance test, the samples were soaked with a 5% w/v HCl solution for 18 h (pH 3–5). For the alkali resistance test, the samples were soaked with a Ca(OH)₂ solution (pH 10–12) for 18 h. The adhesion test was performed by the cross-cut tape method. The surface of the coated samples was scratched into 11 horizontal and 11 vertical grid lines using a cutter. Then, clear adhesive tape was placed on the cross-cut area and pulled in 1 s. The adhesion test results could be observed from the percentages of the removed film, which were classified into six levels, including (5B) not removed, (4B) less than 5%, (3B) about 5–15%, (2B) 15–35%, (1B) 35–65%, and (0B) greater than 65%, respectively. All tests were performed in triplicate.
3.6. Photocatalytic Decomposition of Gaseous Acetaldehyde

The photocatalytic decomposition of gaseous acetaldehyde by the photocatalytic paint was carried out in a closed stainless-steel reactor (volume 54 L) equipped with two 16 W LED visible lamps (wavelength 365–800 nm) and two 220 V blower fans for simulating air circulation (see Figure 13). Two pieces of 24 cm × 24 cm glass plates and two pieces of 24 cm × 54 cm with a total area of 1872 cm² were coated with 300 mL of the photocatalytic paint and placed beside the walls in a closed stainless-steel reactor. The reactor was loaded with gaseous acetaldehyde (50 ppm) in the dark. To determine the adsorption capacity, gas samples were collected every hour to evaluate the acetaldehyde concentration by gas chromatography with a flame ionisation detector (GC-FID, model GC-14B, Shimadzu, Kyoto, Japan). When the adsorption was completed, two LED lamps were turned on and acetaldehyde gas was collected and analysed using GC-FID every hour to determine the photodegradation efficiency.
S.C. was in charge of a research supervisor and acted as a corresponding author upon reasonable request. T.A. was responsible for the data validation. S.S. was responsible for conducting the experiments and preparing the manuscript. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The datasets generated during the current study are available from the corresponding author upon reasonable request.

Conflicts of Interest: All authors declare no conflict of interest.
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