

Rational design of TiO₂-nanocarbon hybrids for photocatalytic applications

by

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B.E., Southern Technical University, 2011
M.S., University of Missouri Columbia, 2016

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Abstract

Environmental pollution and the subsequent impact on human health are major challenges facing our planet. Photocatalysis is one potential strategy for practical, economical, and effective environmental remediation. Among various photocatalysts, hybrid structures formed by coupling TiO_2 and nanocarbons have shown promise in air purification. However, the activity of currently available TiO_2 -nanocarbon hybrids is plagued by the poor interfacial contact between TiO_2 and the nanocarbons, low transparency of the nanocarbons, ineffective adsorption of pollutants on the hybrid photocatalysts, and a large band gap of TiO_2 (3.2 eV), as well as difficulties associated with TiO_2 -nanocarbon synthesis. This study (1) demonstrates the rational design of TiO_2 -nanocarbon hybrids to overcome the aforementioned challenges and (2) investigates the application of designed photocatalysts in environmental photocatalysis.

Among various nanocarbons, metallic carbon nanotubes (CNTs) and MXenes have been widely used as co-photocatalysts with TiO_2 . Due to their highly conductive nature and suitable band structure, these nanostructures can accept charge carriers from TiO_2 , hindering electron-hole recombination and boosting photocatalytic reaction. The first part of my work demonstrates the design of TiO_2 -CNT hybrids with high-quality of interfacial contact and superior photocatalytic activity. We demonstrate that adapting the dimension of CNTs to be compatible with TiO_2 improves the quality of interfacial contact between the two components and provides well-tailored channels for charge carrier shuttling and separation. In this regard, we show that wrapping TiO_2 with short-length CNTs, synthesized by ultrasonication-assisted cutting of long-length CNTs, results in a photocatalyst with higher photocatalytic activity in acetaldehyde oxidation ($k = 0.0150 \text{ min}^{-1}$) than the pristine TiO_2 ($k = 0.0073 \text{ min}^{-1}$) and conventional photocatalyst prepared by

coupling TiO₂ with long CNTs ($k = 0.0107 \text{ min}^{-1}$). Interestingly, the activity of TiO₂ coupled with short CNTs outperforms that of state-of-art photocatalyst, TiO₂-nanographene ($k = 0.0125 \text{ min}^{-1}$).

The second portion of my work investigates the utilization of titanium carbide MXene as a co-photocatalyst with TiO₂. The MXene is not only characterized by its high electrical conductivity (higher than that of CNTs/graphene) but also its unique surface chemistry typified by the presence of abundant functional groups (-F, =O, and -OH). These hydrophilic groups render the facile processibility of MXene via wet chemistry and facilitate its interaction with TiO₂. The same functional groups can also serve as anchors for pollutant adsorption. Nevertheless, MXene derived from the conventional methods is a multilayer structure with low transparency, large size (micro-sized structure), and high concentration of fluorine terminals; these factors are detrimental to the photocatalytic process. On the one hand, the low transparency of MXene hinders light penetration to TiO₂ in the TiO₂-MXene hybrid structure, undermining the charge carrier excitation. On the other hand, the large size of MXene compromises its interaction with TiO₂ while its terminal fluorine groups reduce pollutant adsorption on the resulting hybrid. Therefore, in this project, we demonstrate the intercalation of MXene with tetrapropylammonium hydroxide (TPAOH) to simultaneously delaminate the layers into highly transparent nano-sized sheets and reduce fluorine content on their surface. Coupling nano-sized and delaminated MXene sheets, mainly terminated by oxygen-containing groups, with TiO₂ results in a photocatalyst with superior photocatalytic activity in NO_x oxidation than TiO₂ coupled with conventional MXene or TiO₂-MXene photocatalyst fabricated by thermal treatment of MXene. TiO₂ coupled with delaminated, nanosized MXene converts NO to non-toxic products (i.e., nitrate) and demonstrates high NO_x storage selectivity (85 %) and positive DeNO_x index (+ 0.215), in contrast to another photocatalyst

fabricated by coupling fluorine-containing MXene with TiO_2 , which converts NO to toxic NO_2 and demonstrates low NO_x storage selectivity (65 %) and negative DeNO_x index (- 0.055).

Furthermore, building upon our efforts to utilize MXene in practical photocatalysis, the third portion of my work demonstrates a one-step, safe, and facile approach to synthesizing titanium carbide MXene with abundant oxygen-containing groups. This process is based on etching the titanium aluminum carbide MAX using sodium hydroxide in the presence of a delaminating agent (hydrazine). Unlike the conventional process, the process does not utilize hazardous hydrofluoric acid and complex tools, opening an avenue for safe and low-cost synthesis of MXene for catalysis, particularly in photocatalytic NO_x oxidation reaction where oxygen-containing groups are desired.

In addition to CNTs and MXene, graphitic carbon nitride is another promising visible-light-active nanocarbon due to its low cost and ability to form charge carriers under visible light (band gap: ~ 2.7 eV). However, hybrids formed by coupling g- C_3N_4 and TiO_2 demonstrate only limited activity in NO_x oxidation, likely due to their low adsorption capacity. In the fourth part of my work, a macro-mesoporous TiO_2 -g- C_3N_4 hybrid is employed as a photocatalyst in NO_x oxidation. This porous structure boosts NO_x adsorption and storage of NO_x oxidation products while enabling visible light absorption. TiO_2 -g- C_3N_4 hybrid exhibits high NO_x adsorption capacity and converts NO to nontoxic nitrate with minimal formation of NO_2 , evident by its positive DeNO_x index (+74 ppm) in contrast to g- C_3N_4 with a negative DeNO_x (-4 ppm) and TiO_2 with a slightly positive DeNO_x index (+ 15 ppm). Consequently, effective NO_x photooxidation is achieved by TiO_2 -g- C_3N_4 hybrid under visible light.

To further investigate the possibility of utilizing TiO_2 -nanocarbon in visible-light-driven photocatalysis, the final part of my work exhibits a unique, economical, and scalable approach to

synthesize narrow band gap TiO_2 -titanium carbide (TiO_2 -TiC) photocatalysts. This method is based on detonating a mixture of a hydrocarbon (toluene) and a titanium precursor (titanium tetrachloride) with oxygen in a multi-liter chamber to produce scalable amounts of TiO_2 -TiC hybrids. The synthesized TiO_2 -TiC shows noticeable NO_x photocatalytic activity under visible light.

The findings reported in this thesis are expected to boost ongoing efforts to develop efficient TiO_2 -based photocatalysts and provide reliable and cost-effective pathways for environmental remediation.

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Dedication

To my parents, for always loving me and supporting me.

Chapter 1 - Introduction

Among various air pollutants, nitrogen oxides (NO_x : NO and NO_2), ozone (O_3), and particulate matter ($\text{PM}_{2.5}$) severely impact human health and are among the main causes of lung cancer, cardiovascular, and respiratory diseases [1]. Despite the exerted efforts to minimize air pollution, the concentrations of NO_x , O_3 , and $\text{PM}_{2.5}$ in major urban cities are yet to meet the guidelines set by environmental protection agencies [2]. NO_x need significant attention as they are not only harmful by themselves but also serve as precursors for O_3 and $\text{PM}_{2.5}$ formation [3]. For example, considerable amount of O_3 in the troposphere forms as a result of the reaction between NO_x and volatile organic compounds (VOCs) [4, 5]. NO_x are primarily generated anthropogenically from processes involving the utilization of nitrogen and oxygen at elevated temperatures, in addition to the likelihood of their formation from natural phenomena such as thunder and lightning [6]. To combat these pollutants, strategies have been suggested such as selective catalytic reduction, electrical discharge, adsorption, absorption, and photocatalysis [7-9].

Photocatalysis is the concept that deals with the chemical reactions initiated on the surface of a semiconductor by light exposure. When photons with adequate energy fall on a photocatalyst, the valence band (VB) electrons promote to the conduction band (CB), leaving electron-holes in their original place. The photogenerated electrons and holes participate in redox reactions on photocatalyst surface with adsorbed oxygen and water molecules to form superoxide and hydroxyl radicals, respectively [10]. These radicals are the key in any photocatalytic reaction as they have the potential to interact with chemical species adsorbed on photocatalyst surface and convert them to different products.

As a photocatalyst featured by its nontoxicity, low cost, excellent chemical and physical properties, and chemical stability, TiO_2 has the potential to be harnessed in sustainable,

economically viable, and nonhazardous photocatalytic-based technologies. However, the photo-reactivity of TiO_2 is limited by the fast recombination of charge carriers. The major portion of the formed electron-hole pairs recombine shortly after light exposure and this, in turn, undermines the ability of TiO_2 to initiate surface reactions [11]. In addition, the relatively large band gap of TiO_2 (~ 3.2 eV) restricts its activity to UV light and hinders its application in visible-light-drive photocatalysis [12]. Furthermore, TiO_2 possesses low adsorption capacity [13] and thereby it is unable to effectively adsorb reactants or store photoreaction products. To overcome these challenges, researchers have investigated various approaches to physically and chemically modify TiO_2 properties. In this regard, recent research finds promise in coupling TiO_2 with nanocarbons. Among various nanocarbons, carbon nanotubes, titanium carbides, and graphitic carbon nitrides have acquired immense attention and shown noticeable performance in environmental remediation.

Metallic carbon nanotubes (CNTs) have demonstrated an appealing role as co-photocatalysts with TiO_2 . CNTs are characterized by their excellent electrical conductivity; therefore, they can accept the photoexcited electrons from TiO_2 upon their coupling. In this scenario, the electrons will be on CNTs while the hole will be on TiO_2 , increasing the concentration of charge carriers available for surface reactions. The phenomenon of electron-hole separation remarkably depends on the quality of interfacial contact between TiO_2 and CNTs. Unfortunately, electron-hole separation in conventional photocatalysts is hampered by the non-uniform interaction between CNTs and TiO_2 [14]. Therefore, an alternative approach to couple TiO_2 with CNTs is needed.

Similar to CNTs, titanium carbide MXene ($\text{Ti}_3\text{C}_2\text{T}_x$; where T is surface functional terminals (= O, -OH, and/or -F)) is featured by its high electrical conductivity and tunable work

function, which makes it possible to utilize $\text{Ti}_3\text{C}_2\text{T}_x$ as a charge carrier reservoir with TiO_2 [15]. Benefiting from its unique surface chemistry represented by the presence of abundant functional groups, $\text{Ti}_3\text{C}_2\text{T}_x$ can be readily dispersed with the capability to resist aggregation in water and a plethora of organic solvents, ethanol, N-methyl-2-pyrrolidone (NMP), and N,N-dimethylformamide (DMF) [16], to name few. This enables numerous possible paths to design TiO_2 - $\text{Ti}_3\text{C}_2\text{T}_x$ with a wide range of solvents. The same functional groups can act as anchors to enforce reactant adsorption on the produced photocatalyst and may enable the uptake of specific chemical species favoring selective photocatalytic reaction [17, 18]. Nevertheless, the impact of functional groups and transparency of MXene on its role as a co-catalyst with TiO_2 is obscure and is generally overlooked by researchers. In addition, the difficulty associated with MXene synthesis represented by the utilization of hazardous hydrofluoric acid is one big challenge associated with employing this unique material in photocatalysis.

While coupling TiO_2 with CNTs and MXene can mitigate electron-hole recombination and may boost selective adsorption of pollutants on photocatalyst surface, benefiting UV-light-driven photocatalysis, efforts towards developing visible-light-active TiO_2 -nanocarbon for air purification are still in an early stage. For example, coupling TiO_2 with a low-cost narrow band gap graphitic carbon nitride (g- C_3N_4) is expected to enable visible light activity. In these hybrids, the g- C_3N_4 absorbs visible light while TiO_2 participates in donating or accepting electrons to or from g- C_3N_4 , increasing the lifetime of charge carriers on photocatalyst surface. However, the low adsorption capacity of g- C_3N_4 and its inability to form holes with high oxidation potential undermine its utilization in photocatalytic reactions. Another strategy to enable visible light activity involves reducing the band gap of TiO_2 through doping with a nanocarbon (i.e., intimate

interaction with CNTs). However, the literature is still lacking a scalable, economical, and effective approach to produce low band gap TiO₂-nanocarbon.

The goal of this study is to (1) conduct fundamental investigations that will lead to a rational framework for the synthesis of TiO₂-nanocarbon hybrid photocatalysts with robust charge carrier separation, efficient light absorption, favorable surface chemistry and adsorption capacity, and high photocatalytic activity; and (2) utilize the synthesized photocatalysts in pollutant degradation including VOCs, dyes, and NO_x abatement. Our strategy is based on altering the chemical and physical properties of the nanocarbons to enable their effective coupling with TiO₂ and adapt the properties of the resulting hybrids for effective and selective photocatalysis. This study is guided by the following objectives:

- 1- Enhance the quality of interfacial contact between TiO₂ and CNTs to develop a photocatalyst with superior activity. The hypothesis is that short-length CNTs can interact more intimately with TiO₂ than traditional long-length CNTs, promoting electron-hole separation and the subsequent photocatalytic activity in VOC removal.
- 2- Investigate the synthesis of highly transparent, oxygen-terminated MXene and coupling the synthesized MXene with TiO₂ to enable effective TiO₂-photon interaction and selective pollutant (i.e. NO_x) adsorption on the hybrid photocatalyst during the reaction.

For the MXene synthesis, two hypotheses were tested. The first is that intercalating the MXene with a large-size basic molecule (tetrapropylammonium hydroxide) leads to MXene delamination and, at the same time, fluorine reduction. The second is that the etching the MAX phase by non-fluorine-containing etchants (sodium hydroxide) in the presence of a delaminating agent (hydrazine) results in one-step formation of fluorine-free, delaminated Ti₃C₂T_x sheets.

For the photocatalytic reaction, the hypothesis is that the transparent MXene allows effective light penetration to TiO_2 upon their coupling, ensuring the formation of high concentration of charge carriers on the surface of the hybrid photocatalyst. On the other hand, the presence of oxygen-containing groups on MXene surface fosters selective adsorption of pollutants (NO_2) on photocatalyst surface, facilitating their subsequent oxidation to nitrate.

- 3- Design a hierarchical macro-mesoporous structure composed of TiO_2 -g- C_3N_4 hybrid embedded in parallel TiO_2 channels. The hypothesis is that this unique structure provides efficiently aligned macroporous channels and mesoporous walls for NO_x adsorption while enabling visible light absorption.
- 4- Develop a one-step, economical, and scalable approach to produce visible light active photocatalysts. The hypothesis is that detonating a mixture of titanium precursor (titanium tetrachloride) and carbon precursor (toluene) in a milli-liter reactor results in the formation of TiO_2 -nanocarbon (TiO_2 -titanium carbide) with a narrow band gap, enabling the practical application of visible-light-driven NO_x oxidation.

This work is expected to provide an in-depth understanding of the role played by the nanocarbons as co-photocatalysts with TiO_2 and design well-tailored and effective TiO_2 -nanocarbon hybrids. The broad applicability of this work includes (1) providing effective and novel approaches for the synthesis of nanocarbons with chemical and physical properties desired in photocatalysis and (2) establishing a rational basis for coupling nanocarbons with TiO_2 and improving the performance of TiO_2 -nanocarbon hybrids.

Chapter 2 reports a new approach for improving the interfacial contact and delaying charge carrier recombination in TiO_2 -CNTs hybrid. This approach is based on wrapping short single-wall carbon nanotubes (SWCNTs) on TiO_2 particles (100 nm) via a hydration-condensation technique.

Short SWCNTs with an average length of 125 ± 90 nm are obtained from an ultrasonication-assisted cutting process of pristine SWCNTs ($1 - 3\mu\text{m}$ in length). In comparison to conventional TiO_2 -SWCNT composites synthesized from long SWCNTs ($1.2\pm 0.7\mu\text{m}$), TiO_2 wrapped with short SWCNTs shows longer lifetimes of photogenerated electrons and holes, as well as superior photocatalytic activity. In addition, upon comparison with a TiO_2 -nanographene "quasi-core-shell" structure, TiO_2 -short SWCNT structure offers better electron-capturing efficiency and slightly higher photocatalytic performance, revealing the impact of graphitic structure dimensions on the interfacial transfer of electrons and light penetration to TiO_2 . The engineering of TiO_2 -SWCNT structure is expected to provide alternative pathways to further improve the efficiency of other carbon-based photocatalysts.

Chapter 3 builds upon the insights gained from Chapter 2 and investigates the synthesis of ultrathin, nano-sized $\text{Ti}_3\text{C}_2\text{T}_x$ with abundant oxygen-containing groups ($=\text{O}$ and $-\text{OH}$) and high transparency (designated as $\text{N-Ti}_3\text{C}_2\text{T}_x$) as a co-photocatalyst that can intimately interact with TiO_2 , not only to hinder electron-hole recombination but also to adapt photocatalyst surface chemistry for effective pollutant adsorption. $\text{N-Ti}_3\text{C}_2\text{T}_x$ is prepared by a two-step process that involves etching Al from Ti_3AlC_2 via fluorine treatment followed by simultaneous exfoliation and fluorine reduction via tetrapropylammonium hydroxide treatment. $\text{N-Ti}_3\text{C}_2\text{T}_x$ is then coupled with TiO_2 via a hydration and dehydration approach to form a photocatalyst ($\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$) with distinct morphology and surface chemistry. The small size of $\text{N-Ti}_3\text{C}_2\text{T}_x$ facilitates a strong interfacial contact with TiO_2 , thereby enhancing electron transport between TiO_2 and $\text{N-Ti}_3\text{C}_2\text{T}_x$, and electron-hole separation; the high transparency of $\text{N-Ti}_3\text{C}_2\text{T}_x$ facilitates photon- TiO_2 interaction; and the presence of abundant $=\text{O}$ and $-\text{OH}$ groups on $\text{N-Ti}_3\text{C}_2\text{T}_x$ enables effective pollutant adsorption. As a consequence, the photocatalytic activity of $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ is superior

to that of pristine TiO_2 , TiO_2 coupled with thin, micro-sized $\text{Ti}_3\text{C}_2\text{T}_x$ that is characterized by low transparency and fluorine terminals, and the widely used $\text{Ti}_3\text{C}_2\text{T}_x$ -based photocatalyst synthesized by thermal nucleation of TiO_2 on $\text{Ti}_3\text{C}_2\text{T}_x$.

Since Chapter 3 illuminates the potential of utilizing thin, transparent, and oxygen-containing groups MXene as an efficient cocatalyst with TiO_2 , a facile and safe approach for the synthesis of MXene that would enable its utilization in practical environmental remediation is needed. Therefore, Chapter 4 reports a one-step process to synthesize delaminated, OH-terminated MXene ($\text{Ti}_3\text{C}_2\text{-OH}$) via hydrazine decomposition at 180 °C during an alkali-aided aluminum etching. We demonstrate that the intercalation of hydrazine or its derivatives between Ti layers during the etching process hinders the stabilization of the layers and, in turn, results in delaminated $\text{Ti}_3\text{C}_2\text{-OH}$. When coupled with commercial TiO_2 , $\text{Ti}_3\text{C}_2\text{-OH}$ shows a strong synergistic effect as a cocatalyst in photocatalytic abatement of gaseous NO_x ; excellent NO_x storage selectivity (91%) and a positive DeNO_x value (+ 0.30) are achieved with a reasonable NO conversion (54%). The photocatalytic activity of the hybrid shows high sensitivity to the surface chemistry of the cocatalyst as OH-terminated Ti_3C_2 outperforms delaminated, F-terminated Ti_3C_2 , which shows low NO_x storage selectivity (65 %) and negative DeNO_x value (-0.055). These findings present a novel approach to fabricate delaminated, OH-terminated Ti_3C_2 in a one-step process and suggest the utilization of Ti_3C_2 as an effective co-photocatalyst for NO_x abatement.

While Chapters 2, 3, and 4 deal with UV light-based photocatalysis, Chapter 5 focuses on visible light-derived photocatalysis. Chapter 5 reports the synthesis of a hierarchical macroporous structure composed of Z-scheme $\text{TiO}_2\text{-g-C}_3\text{N}_4$ hybrid embedded in parallel TiO_2 channels as a high adsorption capacity and low band gap photocatalyst for NO_x oxidation. This unique structure provides efficiently aligned macroporous channels and mesoporous walls for NO_x

adsorption and storage of NO oxidation products while enabling visible light absorption. NO_x oxidation is conducted in a laminar-flow reactor under 50 % relative humidity and simultaneous exposure to blue and green lights (cyan light). TiO₂-g-C₃N₄ shows NO conversion (37 %) that is four times higher than that of TiO₂ (7 %) and two times higher than that of g-C₃N₄ (17%). In addition, TiO₂-g-C₃N₄ hybrid exhibits high NO_x adsorption capacity and converts NO to nontoxic nitrate with minimal formation of NO₂, evident by its positive DeNO_x index (+74 ppm) in contrast to g-C₃N₄ with a negative DeNO_x (-4 ppm) and TiO₂ with a slightly positive DeNO_x index (+ 15 ppm). The study demonstrates the delicate relationship between H₂O adsorption on the hybrid structure and NO_x photooxidation reaction and provides detailed mechanistic insights on the photocatalytic response.

Chapter 6 reports a one-step, scalable, economical, and totally new process to synthesize narrow band gap TiO₂-TiC shell-core structure. Our approach is based on detonating a mixture of hydrocarbon (toluene) and titanium precursor (titanium tetrachloride) with oxygen in a multi-liter chamber to produce around seven grams of TiO₂-TiC shell-core structure per second. The synthesized shell-core structure demonstrates noticeable NO_x oxidation under visible light.

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Chapter 2 - Enhanced Charge Separation in TiO₂/Nanocarbon Hybrid Photocatalysts through Coupling with Short Carbon Nanotubes

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2.1 Introduction

Rapid recombination of photogenerated electron-hole pairs is one of the major limitations of utilizing TiO₂ photocatalysts in applications such as water treatment [1-3], air purification [4-9], bacterial and viral inactivation [10, 11], and self-cleaning surfaces [12-14]. Most of the photogenerated electron-hole pairs recombine within 10 picoseconds (ps), which is very short compared to the 100 ps typically required for redox reactions. As a result, only a small portion (~10 percent) of the photogenerated charges, as revealed by time-resolved absorption spectroscopic studies, remain alive and able to participate in pollutant decomposition, resulting in limited photocatalytic activity [15, 16]. A number of studies have shown that inhibition of charge recombination and remarkable enhancement in photocatalytic efficiency of TiO₂ can be achieved by coupling with carbon nanomaterials such as carbon nanotubes (CNTs), graphene, and fullerene [17-21]. The coupling leads to formation of a Schottky barrier, through which electrons efficiently travel from TiO₂ with a higher Fermi level to the carbon nanomaterial with a lower Fermi level until equilibrium is attained [22, 23]. In addition, due to their high electron-storage capacity (one electron per 32 carbon atoms), the graphitic structure can serve as electron reservoirs or sinks,

decreasing the recombination probability of the photogenerated charges in the hybrid material and enhancing photocatalytic activity [22].

The improved charge separation in TiO₂-nanocarbon hybrid structures depends largely on the quality of interfacial contact between TiO₂ and the graphitic structure, and the structural and surface properties of the hybrid components [21, 24-30]. A knowledge gap that still exists is how the graphitic structures and their geometries affect the coupling and interfacial contacts of the components in the hybrid. The rate of electron transport and subsequent separation of photogenerated charges in conventional TiO₂-nanocarbon hybrids are still hampered by nonuniform coating or poor dispersion induced by TiO₂ aggregation on graphene sheets or CNT walls. Therefore, in light of the great promise shown by TiO₂-nanocarbon hybrids in photocatalysis, research efforts have focused on tailoring the heterojunctions to achieve efficient shuttling of electrons and promote electron-hole separation, as well as induce visible light excitation. It is well-established in the literature that charge recombination is inhibited on a variety of TiO₂-CNT hybrids consisting of a thin, uniform TiO₂ layer on individual multi-walled CNTs (MWCNTs) or TiO₂ aggregates supported on CNTs [29, 31-34]. However, the trade-off relation between electron-hole concentration and separation efficiency in conventional TiO₂-coated CNT hybrids remains a significant impediment to maximizing the photocatalytic activity [28, 35]. To this end, TiO₂ wrapped with graphene has been considered as an alternative to the TiO₂/CNT core-shell (or TiO₂-coated CNT) structure, as the concentration of photogenerated charges can be optimized without sacrificing separation efficiency [19, 36].

Significant differences exist in hybrid structures formed with either CNTs or graphene. Graphene, a two-dimensional (2D) structure with several nanometers of width and high stacking tendency, can generate a "shell-like" structure consisting of several graphene layers on TiO₂,

preventing light penetration [37, 38]. Another complication associated with graphene is the unavoidable electron scattering that may reduce electron transport rate and promote charge recombination [38]. On the other hand, harnessing the one-dimensional (1D) single-wall CNT (SWCNT) structures in TiO₂ hybrids not only provides well-defined routes for electron transport, but also their small size compared to MWCNTs and graphene sheets provides a degree of freedom for optimizing charge separation without compromising light absorption [39-43]. A consensus from the aforementioned studies is that the structure of nanocarbons (i.e., the size of graphene or length of CNTs) is a crucial factor in controlling the quality of interfacial contact and subsequent charge separation. In particular, Kim et al.[37] revealed a superior photocatalytic activity for TiO₂ hybrid formed with nano-sized graphene (or nanographene) in comparison to those formed with micro-sized graphene; the wrapping of nanographene on TiO₂ particles in the former hybrid maximized the interfacial contact between the components, resulting in superior charge separation and photocatalytic activity. Similarly, we hypothesize that cutting long SWCNTs into high populations of open-ended tubes with high degrees of functionalization and density of active sites, as well as short lengths that can effectively wrap a large TiO₂ particle (~100 nm), can lead to enhanced interactions with TiO₂ particles that will promote the photocatalytic process. Although many studies have investigated the influence of coupling SWCNTs with TiO₂, all reported works employed SWCNTs with lengths in the micrometer range.

In this study, we report for the first time the wrapping of large TiO₂ particles (~100 nm) with short SWCNTs (125±90 nm in length) obtained from an ultrasonication-assisted cutting process. The resulting TiO₂-SWCNT hybrid photocatalyst exhibits enhanced interfacial contact and charge separation. The short, highly functionalized and dispersed SWCNTs, in the presence of TiO₂, initiated formation of Ti-O-C bonds via intermolecular interactions, resulting in TiO₂

particles or particle aggregates that are partially wrapped by SWCNTs. In comparison to conventional TiO₂-SWCNT hybrid synthesized using long SWCNTs ($1.2 \pm 0.7 \mu\text{m}$), TiO₂ wrapped with short SWCNTs showed longer lifetimes of photogenerated electrons and holes, as well as a superior photocatalytic activity in the gas-phase degradation of acetaldehyde. In addition, upon comparison with a TiO₂-nanographene "quasi-core-shell" structure, the novel TiO₂-SWCNT hybrid offers superior electron-capturing efficiency and slightly higher photocatalytic performance, revealing the impact of the dimension of graphitic structures on the interfacial transfer of electrons and light penetration to TiO₂.

2.2 Experimental Section

2.2.1 Synthesis of TiO₂-SWCNT Hybrids

Purified SWCNTs (1-2 nm in diameter and 1-3 μm in length) were functionalized by refluxing with HNO₃ (70%) at 150 °C for two hours. A known amount of functionalized SWCNTs was dispersed in ethanol and sonicated at 25 °C for four hours to produce the short SWCNTs. After the sonication-assisted cutting process, the resulting suspension was allowed to settle for 15 minutes and the supernatant was slowly added to TiO₂-ethanol dispersion (50 mg in 50 ml distilled water) under sonication, followed by robust stirring overnight at pH = 3.4. The sonicator (Branson, CPX5800H) operated at 100 W and 40 kHz. The TiO₂ particles used had an average crystallite size of 100 nm. The TiO₂-SWCNT hybrid synthesized from short SWCNTs (hereafter referred to as TiO₂-short SWCNT) was collected by filtration using a membrane with average pore size of 0.45 μm and dried at 60 °C. For TiO₂-SWCNT hybrid synthesized from long SWCNTs, the same procedure was followed without subjecting the long SWCNTs to ultrasonication-assisted cutting; the resulting hybrid is hereafter referred to as TiO₂-long SWCNT. Unless stated otherwise, the amount of SWCNTs used in the standard sample is 1 wt%.

2.2.2 Synthesis of TiO₂-Nanographene Hybrid

The graphite powder was oxidized by the modified Hummer method [44]. The graphene oxide (GO) produced was treated with a mixture of HCl and KMnO₄ to produce the nanographene oxide. GO (0.05 g) was dispersed in 50 mL of concentrated HCl, and then 0.05 g of KMnO₄ was slowly added under robust stirring. After one hour of stirring at 40 °C, the resulting slurry was cooled in an ice bath. Then, H₂O₂ solution (5 mL H₂O₂ and 95 mL distilled water) was slowly added with continued stirring for one hour, followed by sonication for 30 minutes to exfoliate the nanographene oxide. The final product was collected by filtration and oven-dried at 60 °C.

The TiO₂-nanographene hybrid (0.7 wt% nanographene) was synthesized by dispersing a known amount of nanographene oxide in ethanol by sonication, and the resulting slurry was slowly added to TiO₂-ethanol dispersion (50 mg in 50 mL distilled water) under stirring at pH = 3.5, followed by robust stirring overnight. The brownish powder obtained was transferred to a Teflon-lined, hydrothermal synthesis autoclave reactor and heated at 120 °C for 24 hours to reduce the nanographene oxide. The final product (hereafter referred to as TiO₂-nanographene) was washed repeatedly with 1 M HCl and distilled water, collected by filtration, and dried at 60 °C.

2.2.3 Characterization Methods

X-ray diffraction (XRD) patterns were collected on a Rigaku Miniex II X-ray diffractometer with Cu K α radiation (λ = 1.5418 Å) at 40 kV ° and 40 mA. The Raman spectra were acquired via an iHR550 spectrometer with a laser excitation wavelength of 532 nm. Catalyst morphology was characterized by a field-emission scanning electron microscope (SEM, Hitachi S5200) equipped with energy-dispersive X-ray spectroscopy (EDS), and a transmission electron microscope (TEM, FEI Talos) operating at 200 kV. For TEM analysis, a small amount of the sample was dispersed in ethanol by sonication and dropped onto a copper microgrid coated with

lacey carbon film. X-ray photoelectron spectroscopic (XPS) measurements were collected via a Kratos Ultra XPS system at 1.0×10^{-9} Torr. A monochromatic Al K α source ($h\nu = 1486.6$ eV) operating at 10 mA and 12 keV (120 W) was used to collect the spectra. The effect of charging was reduced by a charge neutralizer. Survey spectrum was collected at 160 eV pass energy with 1 eV step and 100 ms contact time. For the high-resolution scans, spectra were collected at 20 eV pass energy with 0.1 eV step and 100 ms contact time. The photoluminescence (PL) spectra were acquired via a spectraMax i3x multi-mode microplate reader over the range of 400-700 nm using an excitation wavelength of 360 nm.

2.3.4 Evaluation of Photocatalytic Activity

The photocatalytic activity was tested by measuring the change in concentration of gas phase acetaldehyde as a function of irradiation time. The photocatalyst (100 mg) was placed in a 750-mL borosilicate batch reactor surrounded by light sources, two 25-W Sylvania 21703 (356 nm) bulbs and two 13-W ReptiSun 10.0 UV/B bulbs (280-320 nm). One thousand ppmv of acetaldehyde gas was injected into the reactor via a syringe. After equilibrium between gaseous and adsorbed phases was attained, UV irradiation was started and the decrease in concentration was measured via an SRI 310C gas chromatograph equipped with a Restek silica gel column (8046-895, 6-ft length, 2-mm ID), on-column injection, and flame ionization detector (FID). According to the experimental data, acetaldehyde degradation by TiO₂, TiO₂-long SWCNT, TiO₂-nanographene, and TiO₂-short SWCNT fitted to a pseudo first-order reaction represented by Equation (1):

$$\frac{c}{c_0} = e^{-kt} \quad (2.1)$$

where k is the apparent constant of reaction rate, c is the concentration of acetaldehyde, and t is the reaction time.

2.3 Results

2.3.1 Morphology, Structure, Composition, and Interfacial Properties

The SEM image in Figure 2.1a reveals TiO_2 particles are partially wrapped by short SWCNTs (TiO_2 -short SWCNT), a phenomenon that occurs uniformly over a number of TiO_2 particles. EDS mapping of TiO_2 -short SWCNT (Figure 2.1b) reveals the co-existence of carbon, titanium, and oxygen, with atomic concentrations of 15.75%, 34.23%, and 32.62 %, respectively. The partial wrapping of TiO_2 particles by individual SWCNTs or SWCNT bundles is further confirmed by the TEM images in Figures 2.1c and d while the low-magnification SEM image in Figure A2.1a demonstrates the wrapping phenomenon occurs across a large area of the sample. The TEM images (Figure 2.1c-d) show short SWCNTs of different lengths either as bundles or isolated nanotubes on a TiO_2 particle. From SEM and TEM data, it is apparent intimate interactions between the SWCNTs and TiO_2 exist. The high-resolution TEM images in Figure A2.1b show the SWCNTs form a network on TiO_2 particles. The small diameters of SWCNTs (~ 1.5 nm) compared to that of TiO_2 particles (~ 100 nm) implies a large fraction of the incident light can participate in excitation of TiO_2 . In other words, the deposition of the short SWCNTs does not appear to lead to significant light scattering or prevent light absorption by TiO_2 . However, aggregation of the short SWCNTs was observed in photocatalyst samples with higher SWCNT concentrations as shown in TiO_2 -short SWCNT sample with 3 wt.% SWCNTs (Figure A2.2).

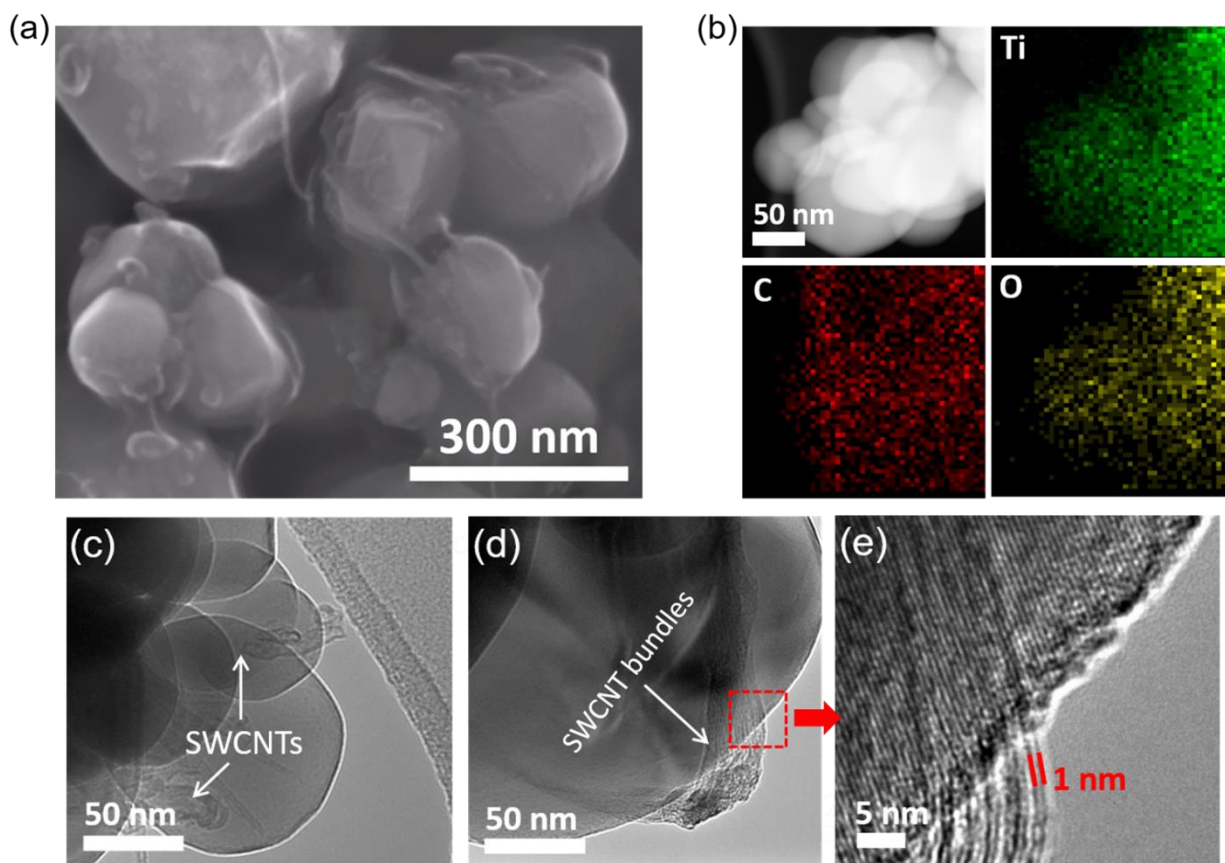


Figure 2.1 (a) SEM image of TiO₂-short SWCNT; (b) EDS mapping of TiO₂-short SWCNT; and (c), (d), and (e) TEM images of TiO₂-short SWCNT showing TiO₂ particles decorated with SWCNT bundles with arrows showing interactions between a TiO₂ particle and SWCNT bundles. Reprinted from reference [35]. Copyright Royal Society of Chemistry 2021.

XRD patterns of short SWCNTs, TiO₂, and TiO₂-short SWCNT are shown in Figure 2.2a. The peaks at $2\theta = 55.1^\circ$, 54.0° , 48.1° , 37.9° , and 25.4° are respectively indexed to (211), (105), (200), (004), and (101) facets, typical for anatase TiO₂. The sharp and intense peaks affirm the high crystallinity of the photocatalysts, whereas the absence of peaks associated with impurities is evidence of their high quality. The peaks at 26.8° and 42.8° , usually attributed to (002) and (100) crystal planes of SWCNTs, were not detected in TiO₂-short SWCNT, due to the low SWCNT concentration (1 wt. %). However, the addition of SWCNTs slightly reduced the relative intensity

of TiO₂ peaks, an observation consistent with other studies [45, 46]. Raman spectra (Figure 2.2b) show the characteristic peaks of anatase TiO₂ at 397, 515, and 639 cm⁻¹ [47]. The characteristic anatase peaks were observed in TiO₂-short SWCNT, accompanied by the disordered carbon-induced D-band at 1350 cm⁻¹, and the G-band at 1583 cm⁻¹ that represents sp² carbon from SWCNTs. The slight shift in anatase modes observed in the Raman and XRD spectra generally correlates with the external perturbation by SWCNTs and the corresponding substitution of Ti⁴⁺ by C atoms, resulting in the formation of Ti-O-C bonds in the TiO₂ lattice [48-51]. However, band gaps of TiO₂ and TiO₂-short SWCNT (calculated from UV-Vis spectra in Figure A2.3) are 3.22 and 3.19 eV, respectively, suggesting low-carbon doping in the hybrid.

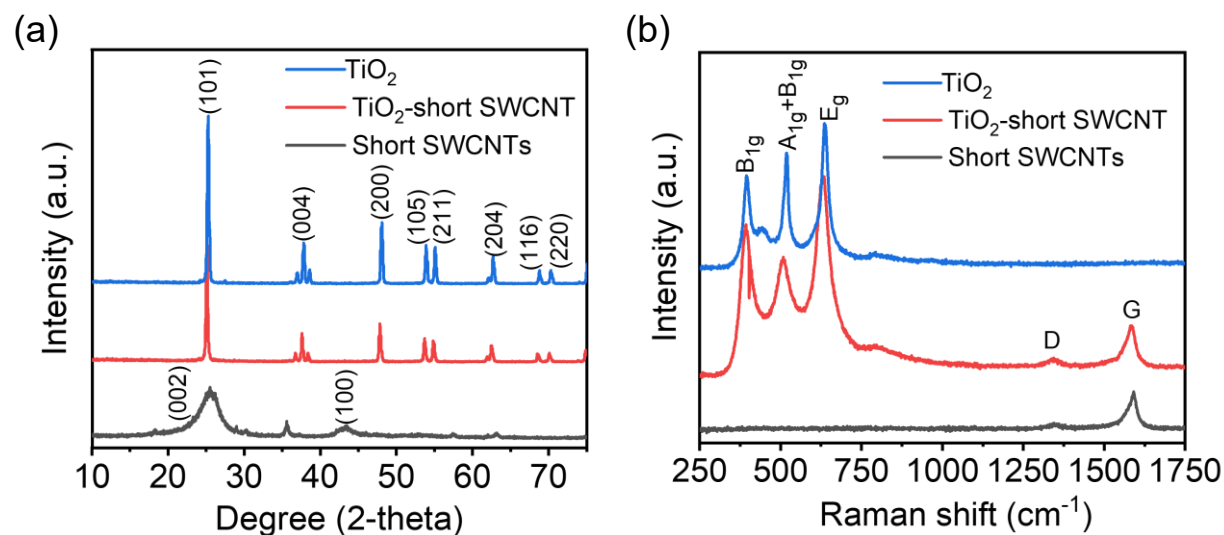


Figure 2.2 (a) XRD profiles of TiO₂, TiO₂-short SWCNT, and short SWCNTs. (b) Raman spectra of TiO₂, TiO₂-short SWCNT, and short SWCNTs. Reprinted from reference [35]. Copyright Royal Society of Chemistry 2021.

An XPS survey spectrum of TiO₂-short SWCNT confirms the presence of Ti, O, and C (Figure 2.3a). The high-resolution XPS spectrum of Ti 2p (Figure 2.3b) shows two peaks located at 459.5 and 465.2 eV attributed to Ti 2p_{3/2} and Ti 2p_{1/2}, respectively, which are typical binding energies of the Ti⁴⁺ valance state [52]. The O 1s spectrum, shown in Figure 2.3c, is fitted with three peak components. The component at 530.7 eV corresponds to Ti–O–Ti, while the peak at 531.6 eV is attributed to C=O or C–OH [52]. The peak at 532.8 eV is ascribed to Ti–O–C, and is an indication of the covalent interaction between TiO₂ and SWCNTs [53]. Based on density functional theory calculations [54], Ti–O–C bonds facilitate charge carrier separation due to their higher electrostatic density in comparison to the non-covalent interaction. As a consequence, the charge redistribution map predicts a higher rate of electron transport. The C 1s region, shown in Figure 2.3d, is fitted with four peak components. The peak at 284.5 eV is assigned to sp² carbon, while the peaks at 285.7, 287.7, and 289.8 eV are assigned to functional groups linked to the carbon atoms including C–O/C–O–Ti, C=O, and O–C=O, respectively [53, 55]. The various oxygen functional groups generate anchors for direct linking with TiO₂. The absence of the Ti–C peak, typically located at 281 eV[56], confirms our claim regarding the absence of carbon doping in the hybrid.

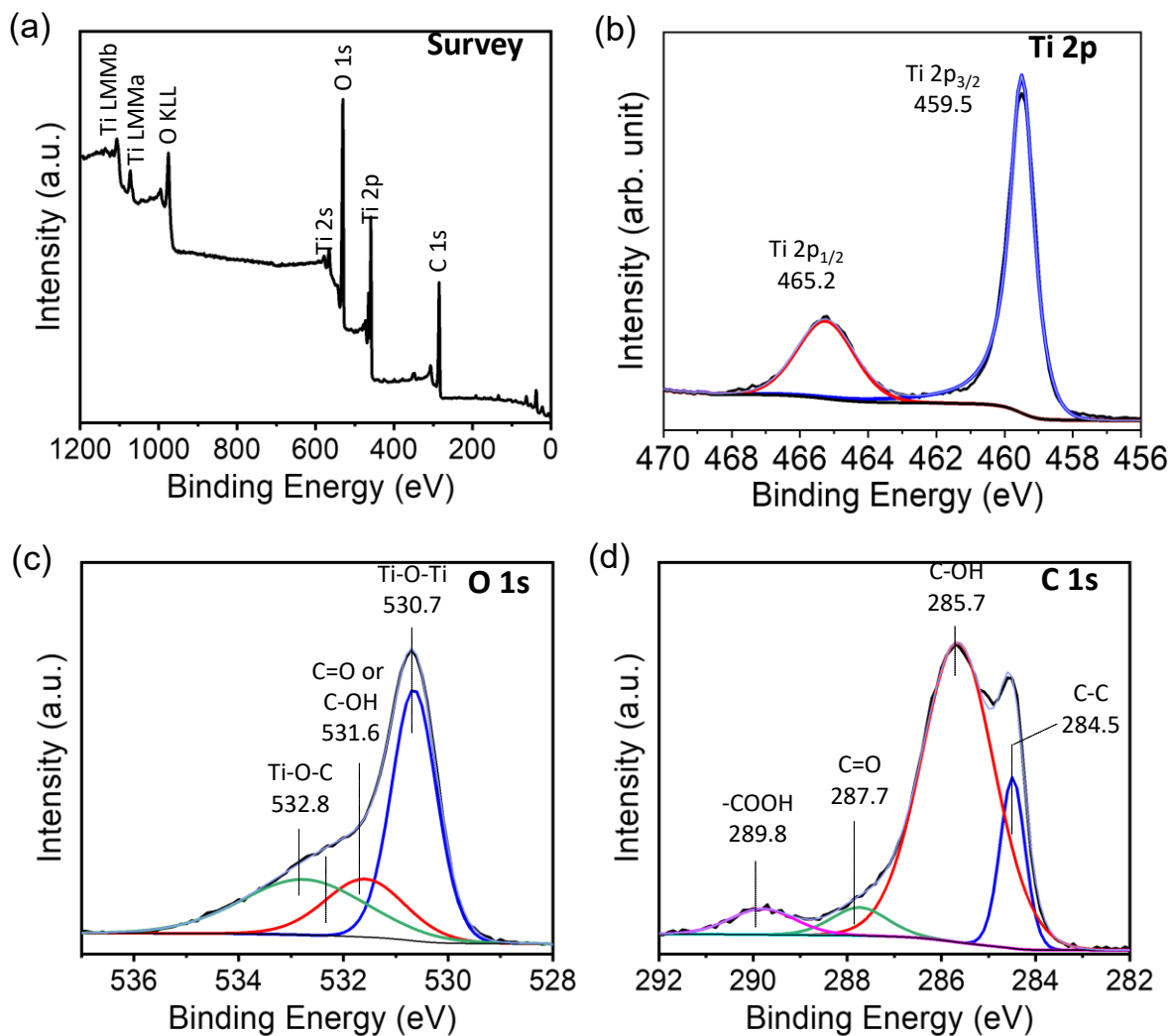


Figure 2.3 XPS spectra of TiO_2 -short SWCNT. XPS survey spectrum (a); deconvolution of high-resolution Ti 2p spectrum (b), O 1s spectrum (c), and C 1s spectrum (d). Reprinted from reference [35]. Copyright Royal Society of Chemistry 2021.

2.3.2 Photocatalytic Degradation of Gaseous Acetaldehyde by TiO_2 -SWCNT Hybrids

To evaluate the photocatalytic activity of TiO_2 wrapped with SWCNTs, the degradation of acetaldehyde was conducted under UV light. Figure 2.4a shows the effect of SWCNT amount in the hybrid structure on photocatalytic activity expressed in terms of normalized acetaldehyde concentration after 60 minutes. Coupling of short SWCNTs with TiO_2 markedly improves degradation of acetaldehyde. The photocatalytic degradation activity is sensitive to the amount of

SWCNTs in the hybrid; our findings revealed the optimum amount to be 1 wt.%. A schematic illustration of the proposed mechanism for photocatalytic degradation of gaseous acetaldehyde on TiO₂-short SWCNT hybrid is depicted in Figure 2.4b along with a summary of reaction schemes [57-60]. Upon light illumination, photo-induced electron-hole pairs are produced by TiO₂; the electrons are promoted to the conduction band leaving holes in the valence band [60]. Since the work function of SWCNTs is lower than the conduction band of TiO₂, SWCNTs can act as electron sinks whereby a fraction of the photoelectrons flow to them [42]. The holes in the valence band react with water molecules to generate hydroxyl radicals ($\cdot\text{OH}$), while the photoexcited electrons in SWCNTs and in the conduction band of TiO₂ react with O₂ to produce superoxide radicals ($\cdot\text{O}_2^-$). The active radicals initiate decomposition of adsorbed gaseous acetaldehyde. The acetaldehyde can be oxidized to acetic acid by $\cdot\text{OH}$ in the first step, and subsequently converted to water and carbon dioxide by $\cdot\text{O}_2^-$ in a second step. $\cdot\text{O}_2^-$ can also oxidize a portion of acetaldehyde directly to carbon dioxide and water.

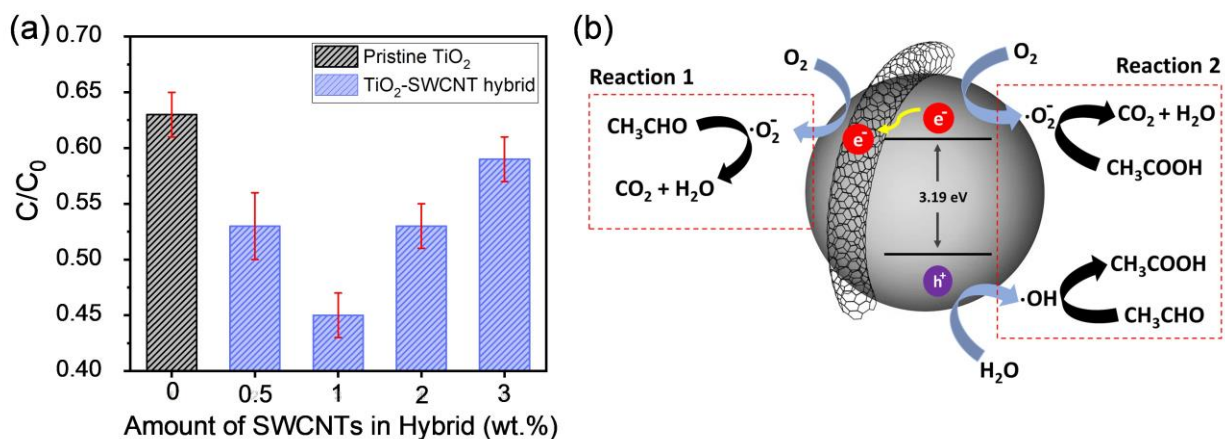


Figure 2.4 (a) Photocatalytic degradation of gaseous acetaldehyde using TiO₂ and TiO₂-short SWCNT of different SWCNT loadings after 60 minutes. (b) Schematic illustration of the possible mechanism of photocatalytic degradation of gaseous acetaldehyde. Reprinted from reference [35]. Copyright Royal Society of Chemistry 2021.

It is well known the photogenerated electron-hole pair participates in redox reactions on catalyst surface to initiate degradation of adsorbed pollutant; however, the process is limited by rapid recombination of electrons and holes. As depicted in Figure 2.4b, one of the roles of SWCNTs in TiO₂-CNT hybrid is to inhibit electron-hole recombination [15, 16]. An increase in the amount of SWCNTs in the hybrid beyond 1 wt.% has a negative effect on the photocatalytic performance, which we attribute to SWCNT aggregation and generation of large SWCNT bundles. The formation of large-diameter bundles indicates SWCNTs at high concentration tend to interact with each other via Van der Waals forces rather than with TiO₂. As a consequence, the quality of interfacial contact (or degree of interaction) between TiO₂ and SWCNTs is reduced. In addition, the coverage of thick SWCNT bundles on TiO₂ particles has the potential of significantly decreasing light penetration to TiO₂, thus reducing photoactivity as observed in other studies that involve wrapping of graphene on TiO₂ or coupling graphene quantum dots with TiO₂ [42, 61]. Despite the decrease in photocatalytic activity upon SWCNT aggregation, the observed performance is still higher than pristine TiO₂, indicating photon permeation is not completely blocked and the beneficial role of SWCNTs in photocatalytic enhancement, via charge separation, may still be partially maintained.

2.3.3 Effect of SWCNT Length and Graphitic Dimension on Interfacial Contact, Charge Separation, and Photocatalytic Activity of the Hybrids

To probe the influence of SWCNT length on the interfacial contact and subsequent photocatalytic performance of TiO₂-SWCNT hybrids, we synthesized another hybrid with long SWCNTs (TiO₂-long SWCNT) using the same concentration of SWCNTs, but without subjecting the sample to the ultrasonication cutting step. Representative TEM images for long SWCNTs and short SWCNTs used for coupling with TiO₂ are presented in Figure A2.4 with corresponding box

plots in Figure 2.5 showing their length distributions; each box plot consists of 12 measurements of nanotubes from TEM images. The average length of short SWCNTs is 125 ± 90 nm while that of long SWCNTs is 1.2 ± 0.67 μ m. The results clearly demonstrate the shear force generated by ultrasonication results in SWCNTs that are significantly shorter than those processed without ultrasonication. The use of ultrasonication as a nondestructive technique for cutting nanotubes is well established in processing nanomaterials. Shuba et al.[62] showed that ultrasonication yields SWCNTs with low side-wall degradation and preserves the electronic properties of the nanotubes. Note that for SWCNTs to efficiently play the intended role of "electron sink" in hybrid structures during photocatalysis, preserving their structural integrity and exceptional electronic properties is critically important.

The Raman spectra of pristine SWCNTs, short SWCNTs, and long SWCNTs in Figure 2.6 provide further insight into the effect of the processing approach on the structure of SWCNTs. The ratio of G- to D-band intensities (I_G/I_D) from the Raman spectra, widely considered a quality or graphitization index for carbon-based materials [63-65], is 13.9 for pristine SWCNTs and decreases to 3.3 and 3.6 after the treatment for long SWCNTs and short SWCNTs, respectively. The I_G/I_D ratios for short and long SWCNTs are about the same, which indicates that the ultrasonication process did not degrade the nanotubes. As observed previously in Figure 2.2b, the TiO₂-SWCNT hybrid exhibited a slight decrease in I_G/I_D , suggesting the increase in defects after the coupling of TiO₂ and SWCNTs [48], probably due to the low substitution of Ti⁴⁺ by carbon atoms. In addition, the characteristic phonon mode in SWCNTs occurring in the low frequency region (zoomed in the insets), the radial breathing mode (RBM), is clearly observed in pristine and processed SWCNTs. In fact, the same RBM peaks for pristine SWCNTs at ~ 150 and 260 cm⁻¹ are

observed for long SWCNTs and short SWCNTs. This provides further evidence that the ultrasonication process did not destroy the nanotubes.

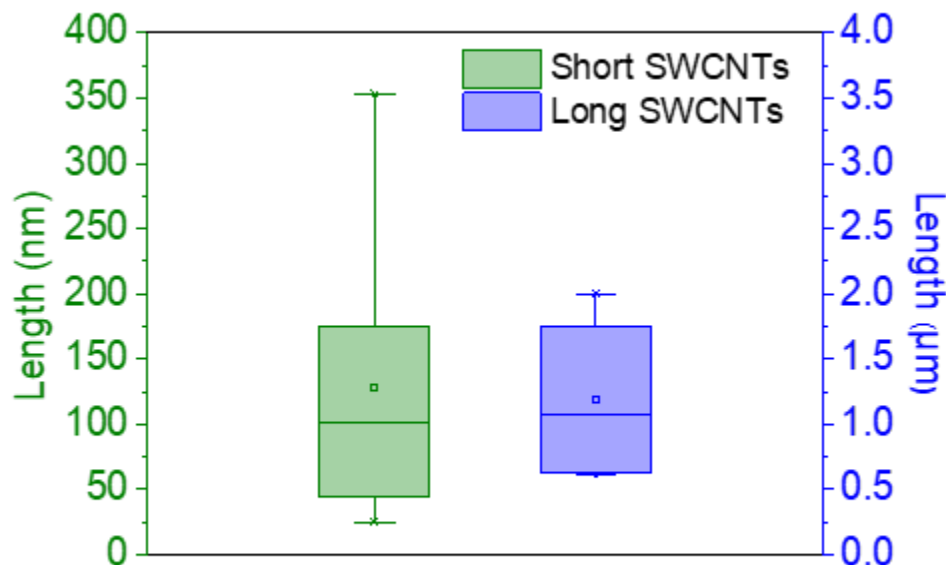


Figure 2.5 Box plots showing lengths of short SWCNTs and long SWCNTs. Each box plot consists of 12 measurements of nanotubes from TEM images. Reprinted from reference [35]. Copyright Royal Society of Chemistry 2021.

Next, we investigate the effect of SWCNT length and nanocarbon dimension on interfacial contact, charge separation, and photocatalytic activity of the hybrids. Electron microscopic images of the resulting hybrids formed with short SWCNTs, long SWCNTs, and nanographene, along with corresponding EDS mapping for TiO₂-nanographene, are shown in Figure 2.7. The EDS mapping of TiO₂-nanographene reveals a highly uniform distribution of titanium, carbon, and oxygen as observed for TiO₂-short SWCNT (Figure 2.1b). In contrast to TiO₂-short SWCNT (Figure 2.7a), bundles of large-diameter SWCNTs are apparent in TiO₂-long SWCNT hybrid (Figure 2.7b), with severe particle aggregation as shown in Figure A2.5. These observations give credence to the assumption that ultrasonication not only reduces the length of SWCNTs, but also

facilitates debundling of SWCNTs. Morphological characterization of micron-sized graphene, exfoliated nanographene, and non-exfoliated nanographene are summarized in Figure A2.6. The average size of the nanographene, as determined from TEM analysis and shown on the box plot (Figure A2.6), is $\sim 125 \pm 93$ nm.

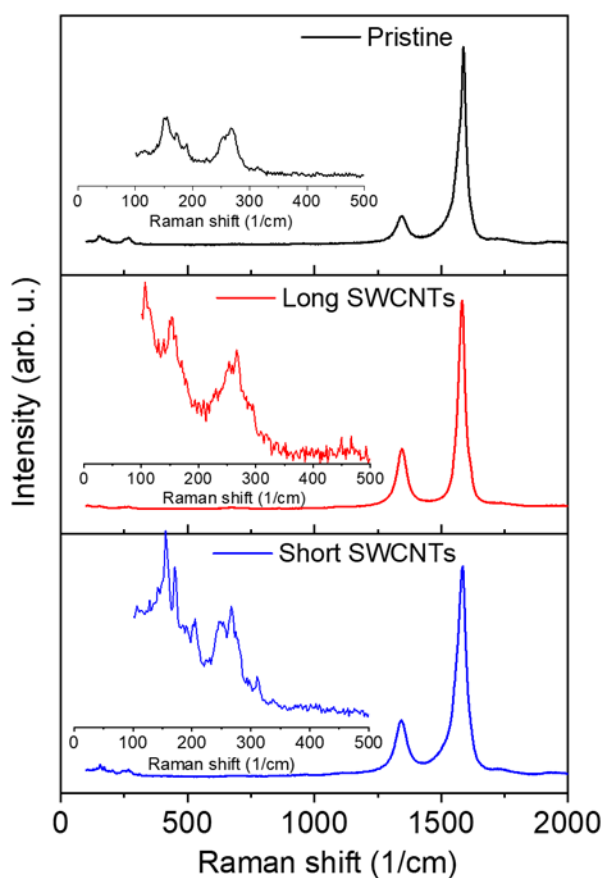


Figure 2.6 Raman spectra of pristine SWCNTs, long SWCNTs, and short SWCNTs with insets showing zoom-in spectra of RBMs in the lower frequency region. Reprinted from reference [35]. Copyright Royal Society of Chemistry 2021.

Photocatalytic degradation of acetaldehyde by TiO_2 , TiO_2 -long SWCNT, TiO_2 -nanographene, and TiO_2 -short SWCNT, is shown in Figure 2.8a along with the PL spectra of the photocatalysts in Figure 2.8b. As depicted in Figure 2.8a, TiO_2 -short SWCNT shows the highest

performance; the rate constant of TiO₂-short SWCNT is 0.015 min⁻¹, while others are given as follows: pristine TiO₂ ($k = 0.0073 \text{ min}^{-1}$), TiO₂-long SWCNT ($k = 0.0107 \text{ min}^{-1}$), and TiO₂-nanographene ($k = 0.0125 \text{ min}^{-1}$). TiO₂-short SWCNT showed better performance compared with TiO₂-nanographene, even though the quality of interfacial contact in the two heterostructures is somewhat similar, as evidenced by EDS mapping that reveals a highly uniform distribution of nanographene on TiO₂ particles over a large area (Figure 2.7d). The PL spectra (Figure 2.8b) show lifetimes of charges on TiO₂ coupled with short SWCNTs are longer than TiO₂ coupled with nanographene, which explains the different photocatalytic activities observed as evidenced by their rate constants.

2.4. Discussion

Based on our results, we present a schematic illustration of the interfacial contact between nanocarbon (short SWCNTs, long SWCNTs, or nanographene) and TiO₂, as well as the charge carrier movement in the hybrids in Figure 2.9. We rationalize the superior performance of TiO₂-short SWCNT to be due to the inhibition of charge recombination in the hybrid, which can be achieved in two ways. First, the increase in the number of heterojunctions between each individual TiO₂ and short SWCNTs provides more channels for electron transport, inhibiting charge recombination. The short and well-exfoliated SWCNTs can have lower bending stiffness compared to the long and non-exfoliated SWCNTs. It has been shown that bending stiffness of SWCNTs is directly proportional to SWCNT diameter [66]; therefore, we expect large-diameter SWCNT bundles to have larger persistence length compared to exfoliated SWCNTs (or small-diameter SWCNT bundles). Hence, short SWCNTs efficiently wrap a TiO₂ particle (Figure 2.9a). Consequently, a large fraction of TiO₂ particles are in direct contact with short SWCNTs. In contrast, only a small fraction of TiO₂ particles are in direct contact with the long SWCNTs.

Second, the improved SWCNT debundling ensures a uniform distribution of SWCNTs over a large area on the TiO_2 surface, and hence, the shuttling of electrons across the interface for enhanced charge separation is not restricted to a small portion of the hybrid as in the case of TiO_2 -long SWCNT hybrid. To test the above hypotheses, PL data presented in Figure 2.8b provide valuable insight. In comparison to pristine TiO_2 , fluorescence quenching was observed in the TiO_2 -SWCNT hybrid, confirming the transfer of electrons from TiO_2 to SWCNTs delayed charge recombination. It is clear from the PL results that the intensity of TiO_2 -short SWCNT hybrid is lower than that of TiO_2 -long SWCNT hybrids, and substantially is lower than pristine TiO_2 , confirming the efficient charge separation occurring in TiO_2 -short SWCNT hybrid.

To rationalize the role of short SWCNTs (or oxygen-containing functionalities), we have to consider the synthesis steps, and in particular, the zeta potentials of SWCNTs and TiO_2 particles in ethanol under the pH used. Factors such as type of solvent and pH of mixture can alter the surface charge of nanostructures. In our case, acid treatment lowers the zeta potential of SWCNTs due to the formation of oxygen functionalities as shown by Liu et al.[67]. These functional groups on the surface and tips of short SWCNTs impart a strong negative charge and make them more easily dispersed. The negatively charged groups provide a strong electrostatic attraction toward positively charged species. Conversely, at low pH or high hydrogen ion activity, the surface of TiO_2 acquires a positive charge due to the high zeta potential. In fact, Widegren and Bergström [68] showed that the addition of a relatively small amount of acid or base is capable of introducing a relatively strong charge on TiO_2 particles. In our synthesis experiment, TiO_2 particles and functionalized SWCNTs were dispersed in ethanol at pH = 3.5 which creates an environment with a high hydrogen activity and a strong positive charge on TiO_2 . The strong positively charged TiO_2 particles and negatively charged functionalized SWCNTs interact strongly via electrostatic

attraction to form the hybrid structures with enhanced interfacial contact. In addition, opened and unblocked CNTs significantly increase the density of adsorption or anchoring sites [69]. Cutting of long SWCNTs increases the number of open ends, and therefore, the short SWCNTs provide more "handles" or anchoring sites for interactions with TiO_2 than long SWCNTs.

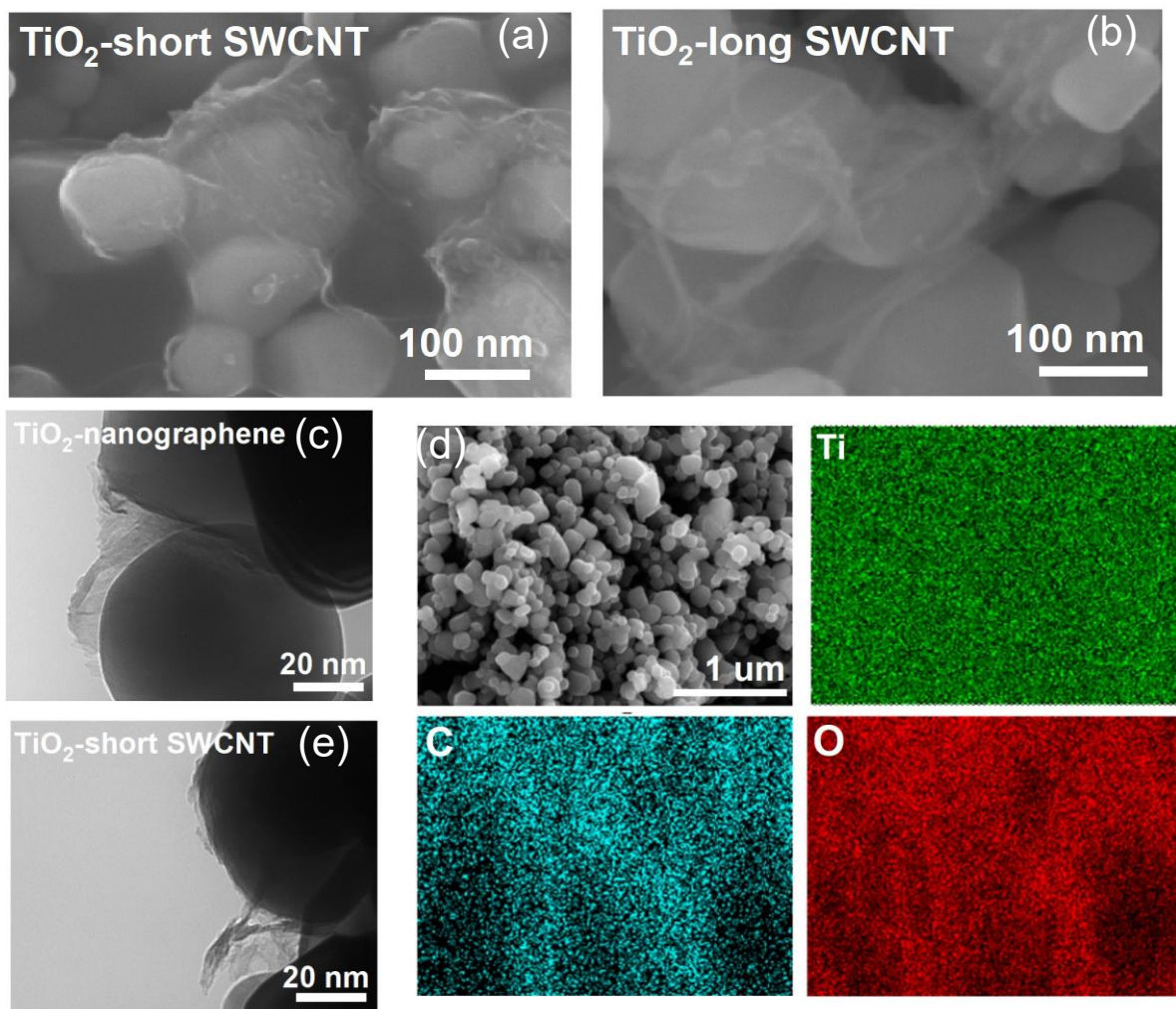


Figure 2.7 SEM images of TiO_2 -short SWCNT (a) and TiO_2 -long SWCNT (b), TEM image of TiO_2 -nanographene (c), SEM image of TiO_2 -nanographene and the corresponding EDS mapping (d), and TEM image of TiO_2 -short SWCNT (e). Reprinted from reference [35]. Copyright Royal Society of Chemistry 2021.

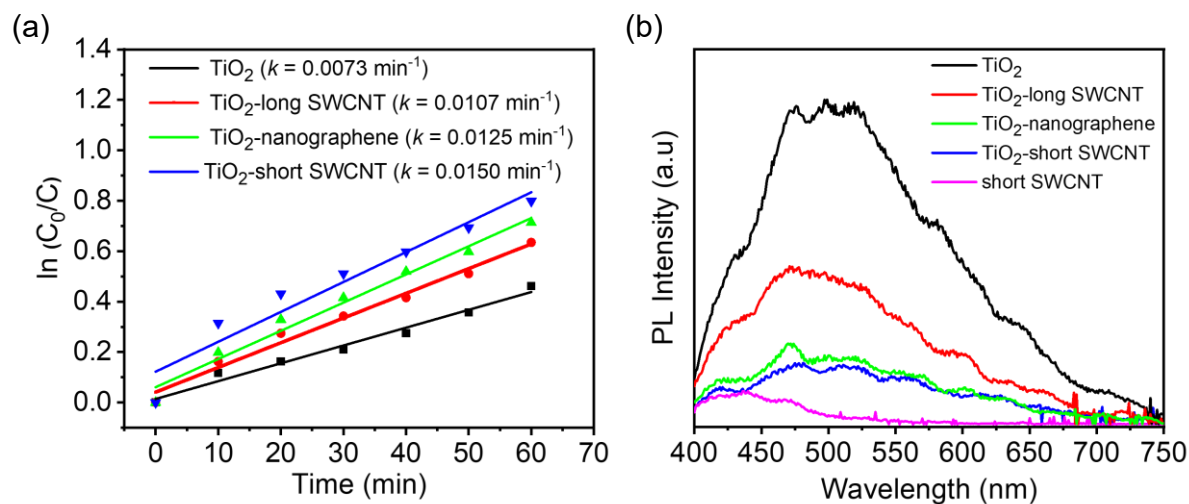


Figure 2.8 (a) Photocatalytic activity of TiO₂, TiO₂-long SWCNT, TiO₂-nanographene, and TiO₂-short SWCNT during degradation of gaseous acetaldehyde based on a pseudo first-order kinetic model. (b) Photoluminescence spectra of TiO₂, TiO₂-long SWCNT, TiO₂-nanographene, and TiO₂-short SWCNT. Reprinted from reference [35]. Copyright Royal Society of Chemistry 2021.

The dimension of the graphitic structure is another important factor that can affect charge separation. To understand the impact of graphitic structure dimension on the photocatalytic activity, we compared the performance of TiO₂ quasi-wrapped by 1D SWCNTs (TiO₂-short SWCNT) with the quasi-wrapped by 2D nanographene (TiO₂-nanographene). The synthesis of the quasi-core-shell structure is adapted from a technique proposed by Kim et al.[37]. We hypothesize that random pathways in 2D graphene can significantly reduce electron transport rate or may lead to electron escape from the graphene sheet (as schematically depicted in Figure 2.9c), and thus promote charge carrier recombination. In contrast, the 1D SWCNTs offer efficient and short pathways for the transfer of vectorial electrons and, hence, enhanced charge separation. In addition, nanographene has a high stacking tendency and even after exfoliation, the number of layers cannot be easily controlled. During TEM analysis, we observed several TiO₂ particles with thick graphitic shells, considerably thicker than SWCNT bundles (see Figure 2.7c and e). This means significant portion of incident light is hindered from reaching TiO₂ in a typical core-shell

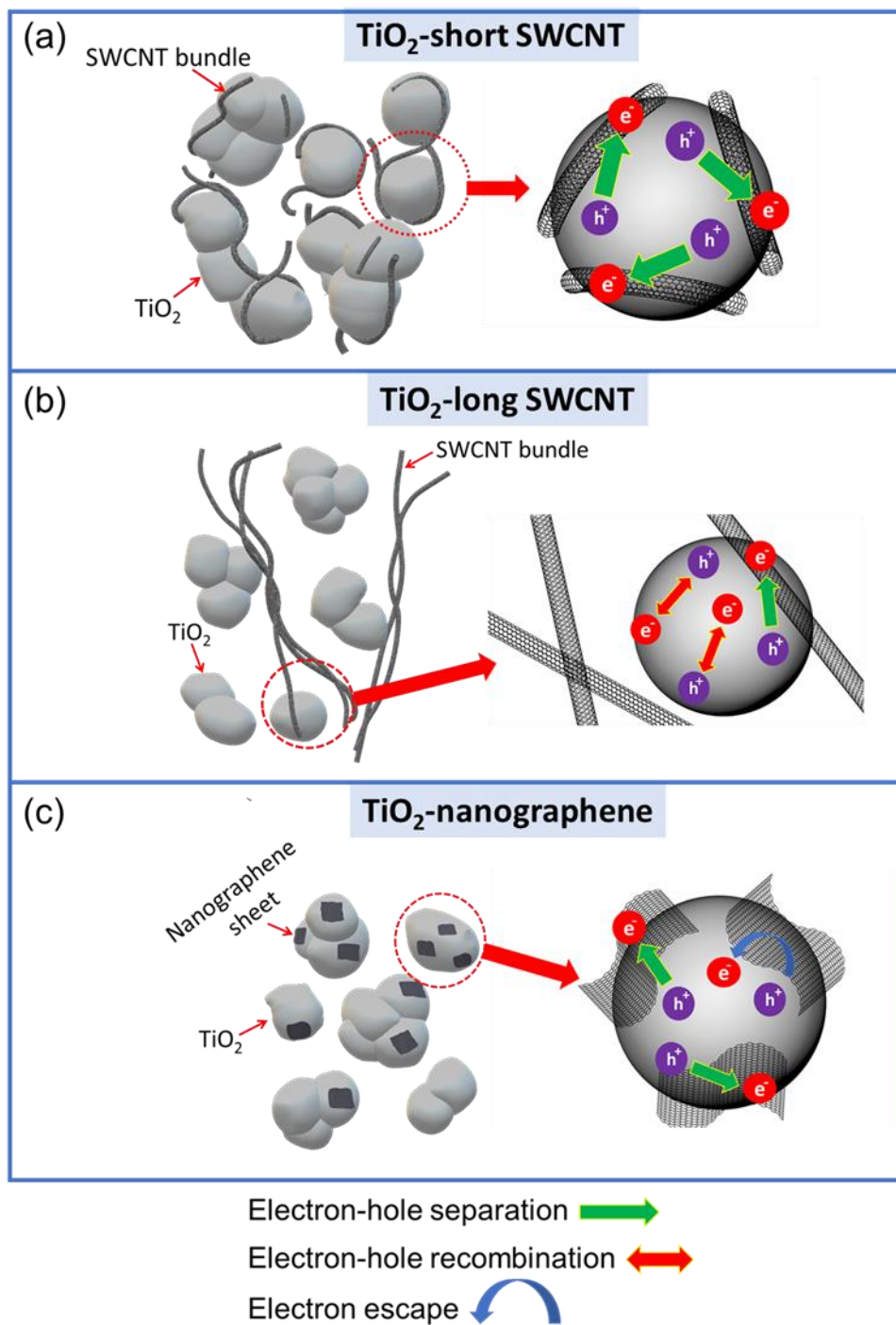


Figure 2.9 Schematic illustrations of charge carrier movement in TiO₂-long SWCNT, TiO₂-short SWCNT, and TiO₂-nanographene. Reprinted from reference [35]. Copyright Royal Society of Chemistry 2021.

structure for TiO₂-nanographene. On the other hand, SWCNTs, even in the case of bundles, due to their one-dimensional structure and small diameters, do not completely block light permeation to TiO₂, as shown earlier for hybrid structures synthesized using high SWCNT concentrations. Nevertheless, coupling short SWCNTs or nanographene significantly improved electron-hole separation and photoreactivity of TiO₂; the photoexcited electrons in the TiO₂ core are efficiently transported into the nanocarbon due to the strong interfacial contact between the hybrid components.

2.5 Conclusions

TiO₂ quasi-wrapped with short SWCNTs was successfully fabricated via an approach that involves the interaction between TiO₂ and short SWCNTs in ethanol as a solvent. The presence of short SWCNTs resulted in enhanced photocatalytic efficiency and efficient charge separation. The improved interfacial contact, verified by electron microscopy, prolonged the lifetime of an electron-hole pair on TiO₂ as demonstrated by photoluminescence spectroscopy. Unlike a hybrid structure with long SWCNTs, higher photocatalytic performance in gas-phase degradation of acetaldehyde was achieved with TiO₂-short SWCNT hybrids, confirming use of short SWCNTs in coupling with TiO₂ as a better alternative. Investigations into the effect of nanocarbon dimension on charge separation revealed TiO₂-short SWCNT hybrid has slightly higher photocatalytic activity than TiO₂-nanographene. We attribute the performance to electron scattering in 2D-nanographene, which may affect electron transport through the heterojunction. The high stacking tendency of nanographene may form a thick graphitic layer on TiO₂ that could hinder light penetration. Overall, this study provides rational new guidelines for maximizing electron-hole separation in TiO₂-nanocarbon hybrids for improved photocatalytic performance.

2.6. References

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Chapter 3 - Synthesis of Ultrathin, Nano-Sized $\text{Ti}_3\text{C}_2\text{T}_x$ with Abundant =O and -OH Terminals and High Transparency as a Cocatalyst: Enabling Design of High-Performance Titania- $\text{Ti}_3\text{C}_2\text{T}_x$ Hybrid Photocatalysts

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3.1 Introduction

Two-dimensional transition metal carbides and nitrides, known as MXenes, have received immense attention since their discovery at Drexel University in 2011 [1]. The general formula of MXenes is $\text{M}_{n+1}\text{X}_n\text{T}_n$, where M is early transition metal, X is carbon or nitrogen, and T is surface functional terminals (= O, -OH, and/or -F). The most widely used MXene is titanium carbide ($\text{Ti}_3\text{C}_2\text{T}_x$) and is characterized by unique properties that are of massive benefit to photocatalysis: (1) high mobility of charge carriers that can promote migration and separation of photoexcited electron-hole pairs [2], (2) Ti sites on $\text{Ti}_3\text{C}_2\text{T}_x$ surface that may provide stronger redox reactivity compared to traditional carbon materials [3], and (3) unique surface chemistry of $\text{Ti}_3\text{C}_2\text{T}_x$ represented by its hydrophilic nature and abundant functional terminals that can adsorb a variety of molecules and ionic species [4, 5]. The distinctive properties of $\text{Ti}_3\text{C}_2\text{T}_x$ highlighted above have impelled the design of $\text{Ti}_3\text{C}_2\text{T}_x$ -based photocatalysts with the aim of increasing charge carrier mobility, reactant adsorption, and surface reactivity. In this regard, numerous $\text{Ti}_3\text{C}_2\text{T}_x$ -based photocatalysts such as $\text{BiOBr-Ti}_3\text{C}_2\text{T}_x$, $\text{CdS-Ti}_3\text{C}_2\text{T}_x$, $\text{Ag}_3\text{PO}_4\text{-Ti}_3\text{C}_2\text{T}_x$, $\text{RuO}_2\text{-TiO}_2\text{-Ti}_3\text{C}_2\text{T}_x$, $\text{g-C}_3\text{N}_4\text{-Ti}_3\text{C}_2\text{T}_x$, and $\text{CuFe}_2\text{O}_4\text{-Ti}_3\text{C}_2\text{T}_x$ have been designed and employed in various applications including water splitting, O_2 production, N_2 fixation, and bacterial inactivation [6-12].

Hybrids formed by coupling $\text{Ti}_3\text{C}_2\text{T}_x$ and TiO_2 have emerged as a promising family of environmental photocatalysts, in which the resulting Schottky junction formed between them leads to effective separation of photo-generated electron-hole pairs, while the functional terminals of $\text{Ti}_3\text{C}_2\text{T}_x$ (particularly, =O and -OH groups) facilitate the adsorption of pollutants on photocatalyst surface and their subsequent degradation. One approach that has been utilized to synthesize TiO_2 - $\text{Ti}_3\text{C}_2\text{T}_x$ hybrid is the nucleation of TiO_2 on $\text{Ti}_3\text{C}_2\text{T}_x$ surface through thermal treatment. The hybrids produced by oxidation of $\text{Ti}_3\text{C}_2\text{T}_x$ at elevated temperatures (160 to 800 °C) have shown noticeable performance in photocatalytic degradation of environmental pollutants [13-18]. However, the conversion of a Ti layer into TiO_2 sacrifices the integrity of $\text{Ti}_3\text{C}_2\text{T}_x$ structure and possibly reduces its ability to accept the photogenerated charge carriers, undermining the benefit of utilizing $\text{Ti}_3\text{C}_2\text{T}_x$ in photocatalysis. As an alternative approach, coupling commercial TiO_2 with thin/layered, micro-sized $\text{Ti}_3\text{C}_2\text{T}_x$ through hydration and dehydration has been used to produce TiO_2 - $\text{Ti}_3\text{C}_2\text{T}_x$ hybrids while preserving the structural integrity of $\text{Ti}_3\text{C}_2\text{T}_x$ [4]. However, the average size of $\text{Ti}_3\text{C}_2\text{T}_x$ used (several hundred nanometers to a few micrometers) in coupling is significantly larger than that of TiO_2 nanoparticles (typically in the range of 20 to 200 nm). This considerable size difference can diminish the quality of interfacial contact between TiO_2 and $\text{Ti}_3\text{C}_2\text{T}_x$, and in turn, impede the mobility of charge carriers in the hybrid. Also, light transmittance of $\text{Ti}_3\text{C}_2\text{T}_x$ is linearly dependent on its thickness that decreases with the number of layers and is independent of wavelength. For instance, a transmittance of 68% was attained by a 17-nm thin film of $\text{Ti}_3\text{C}_2\text{T}_x$, indicating 32% of incident light was absorbed or scattered [19, 20]. The photon interaction with TiO is a critical first step in photocatalysis as it yields the reactive oxygen species; therefore, a cocatalyst that potentially obstructs penetration of photons to TiO_2 is undesired. Furthermore, the conventional $\text{Ti}_3\text{C}_2\text{T}_x$ used in photocatalysis is typically terminated by fluorine groups that are inevitably attached to its surface during the fabrication process. These terminals are undesired as they mitigate the adsorption of pollutants on the surface of MXene-based photocatalysts [4, 21-24]. For the full potential of $\text{Ti}_3\text{C}_2\text{T}_x$ -based photocatalysts to be realized, the

aforementioned challenges that are directly connected to the photocatalytic process would have to be addressed.

A recent study reveals that ultrathin MXene ($\text{Ti}_3\text{C}_2\text{T}_x$ film with thickness of less than 2.5 nm) possesses a transmittance of 90% while returning high conductivity exceeding 6500 S cm^{-1} [25]. Also, a previous investigation involving the coupling of TiO_2 and graphene suggests utilizing a nano-sized graphitic structure as opposed to a micro-sized one as it maximizes the interfacial contact and promotes electron-hole separation [26]. Hence, it is reasonable to hypothesize that coupling ultrathin, nanosized $\text{Ti}_3\text{C}_2\text{T}_x$ and TiO_2 has the potential to maximize the interfacial contact in $\text{Ti}_3\text{C}_2\text{T}_x$ - TiO_2 photocatalysts and promote migration and separation of charge carriers without interrupting photon flux to TiO_2 . Therefore, herein, we demonstrate the synthesis of ultrathin, nano-sized $\text{Ti}_3\text{C}_2\text{T}_x$ (N- $\text{Ti}_3\text{C}_2\text{T}_x$) that is characterized by high transparency and abundant =O and -OH groups (reduced fluorine content), and its subsequent coupling with TiO_2 to produce a hybrid photocatalyst (designated as TiO_2 -N- $\text{Ti}_3\text{C}_2\text{T}_x$). The photocatalytic activity of the photocatalyst was evaluated in liquid phase via methylene blue (MB) degradation and in gas phase via NO_x oxidation. Our results reveal the superior photocatalytic activity of TiO_2 -N- $\text{Ti}_3\text{C}_2\text{T}_x$ in comparison to pristine TiO_2 and TiO_2 coupled with thin, micro-sized $\text{Ti}_3\text{C}_2\text{T}_x$ (TiO_2 -M- $\text{Ti}_3\text{C}_2\text{T}_x$) that is characterized by low transparency and fluorine terminals. Comprehensive morphological, optical, and chemical characterization of the photocatalysts has enabled elucidation of the observed differences in photocatalytic activity. Our findings will benefit current efforts aimed at exploiting the outstanding properties of MXenes in the design of efficient hybrid photocatalysts.

3.2 Experimental Section

3.2.1 Synthesis of M- $\text{Ti}_3\text{C}_2\text{T}_x$ and N- $\text{Ti}_3\text{C}_2\text{T}_x$

The reaction between HCl and LiF was exploited to etch Al from MAX phase (Ti_3AlC_2) and exfoliate the sheets to produce M- $\text{Ti}_3\text{C}_2\text{T}_x$ [27, 28]. 1 g of LiF (Sigma-Aldrich, USA) was added to freshly prepared 9 M HCl (Sigma-Aldrich, USA) aqueous solution. The mixture was stirred for 10

minutes to dissolve the salt, followed by slow addition of 1 g of Ti_3AlC_2 powder (Carbon, Ukraine; particle size: 40 μm). The mixture was maintained at 40 °C for 36 hours. Thereafter, the resulting residue was washed repeatedly with DI water via cycles of centrifugation (10 minutes per cycle at 4000 rpm) until the pH of the supernatant reached approximately 6. The final product was filtered using a nylon filter and dried in air. Tetrapropylammonium hydroxide (TPAOH) treatment was used to further exfoliate the $\text{M-Ti}_3\text{C}_2\text{T}_x$ and produce $\text{N-Ti}_3\text{C}_2\text{T}_x$. 2g of $\text{M-Ti}_3\text{C}_2\text{T}_x$ was immersed in TPAOH (25 wt% aqueous solution; Fisher-Scientific, USA) and stirred for 3 days at room temperature. Thereafter, the resulting residue was collected by cycles of centrifugation with water and dried in air. A schematic illustration of the fabrication process of $\text{M-Ti}_3\text{C}_2\text{T}_x$ and $\text{N-Ti}_3\text{C}_2\text{T}_x$ is shown in Figure 3.1a.

3.2.2 Synthesis of $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$ and $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ Hybrid Photocatalysts

Anatase TiO_2 (100 nm) was first treated with 3-aminopropyl-trimethoxysilane (APTMS; Fisher-Scientific, USA), following the procedure reported by Lee et al. [29], to facilitate the interaction between TiO_2 and $\text{Ti}_3\text{C}_2\text{T}_x$. For synthesis of $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$, two solutions were first prepared. Solution A: 40 mg of TiO_2 was dispersed in 40 mL distilled water by ultrasonication for 50 minutes. Solution B: a specific weight percentage of $\text{M-Ti}_3\text{C}_2\text{T}_x$ (2.5, 5, 10, 15, or 30 wt% with respect to TiO_2) was dispersed in 10 mL distilled water by ultrasonication for 50 minutes. Then, solution B was added dropwise to solution A under stirring and the resulting mixture was stirred for 50 minutes. Thereafter, the $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$ was collected by centrifugation and dried in air. For synthesis of $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$, the same procedure was followed except $\text{M-Ti}_3\text{C}_2\text{T}_x$ was replaced with $\text{N-Ti}_3\text{C}_2\text{T}_x$. The schematic illustration of the fabrication process of $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ is shown in Figure 3.1b. For comparison, $\text{TiO}_2\text{-O-Ti}_3\text{C}_2\text{T}_x$ was also synthesized by calcination of 300 mg of $\text{M-Ti}_3\text{C}_2\text{T}_x$ in air at 450 °C for 4 hours.

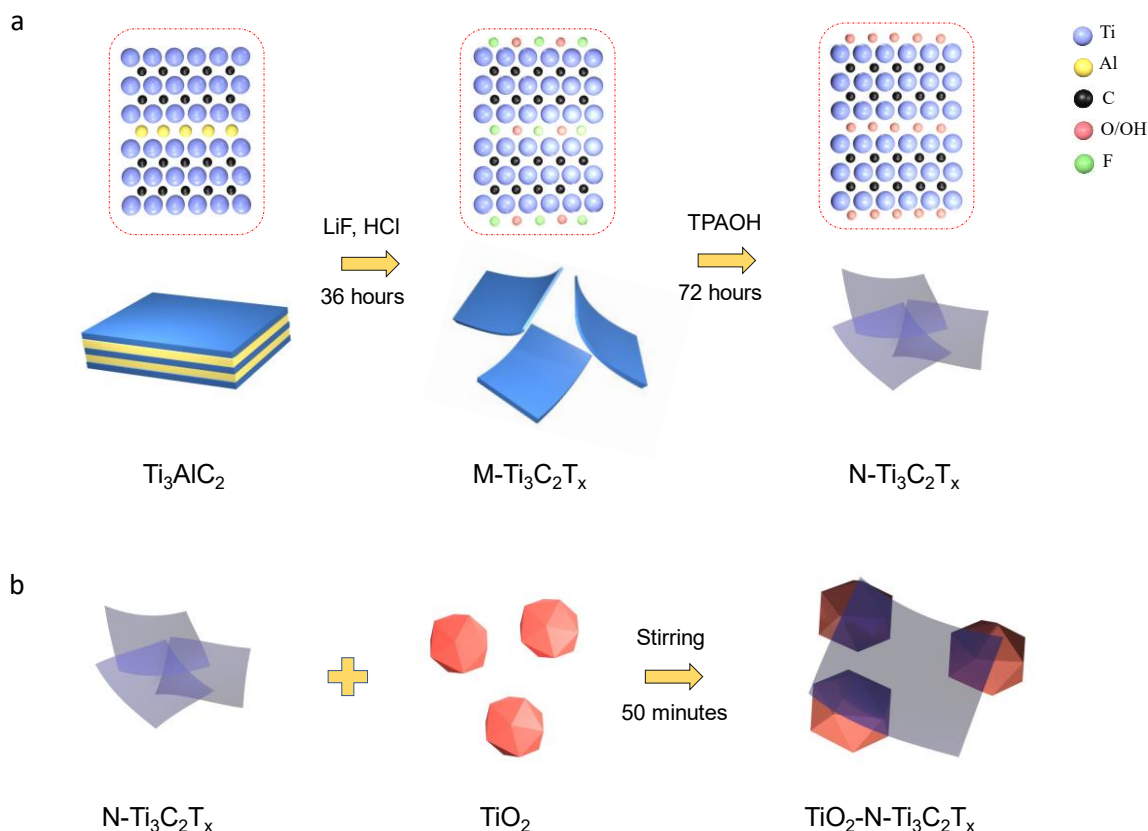


Figure 3.1 Schematic illustrations of the synthesis steps of $\text{M-Ti}_3\text{C}_2\text{T}_x$ and $\text{N-Ti}_3\text{C}_2\text{T}_x$ (a) and $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ (b). Reproduced from reference [24]. Copyright Elsevier 2022.

3.2.3 Characterization

The morphologies of $\text{Ti}_3\text{C}_2\text{T}_x$ and the synthesized photocatalysts were characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM). SEM images were acquired by a Hitachi S4700 II cFEG microscope at an accelerating voltage of 10 kV using the secondary electron detector. TEM images were captured by a Thermo Fisher Scientific G2 Tecnai F30 FEG high-resolution microscope. For TEM imaging, a small amount of the sample was dispersed in ethanol by ultrasonication and drop cast on a copper microgrid coated with lacey carbon. The images were acquired at an accelerating voltage of 300 kV. Fourier transform infrared (FTIR) spectroscopy was exploited to detect the presence of functional groups on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ and the hybrid

photocatalysts. FTIR spectra were recorded on a Cary 630 Agilent spectrometer at a resolution of 4 cm^{-1} . Raman spectroscopy was utilized to study the compositions of $\text{Ti}_3\text{C}_2\text{T}_x$ and the hybrid photocatalysts. Raman spectra were obtained by Renishaw Invia Raman microscope with an excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) was used to probe the surface chemistry of $\text{Ti}_3\text{C}_2\text{T}_x$ and the hybrid photocatalysts. XPS data were collected using a PHI 5000 VersaProbe II (Physical Electronics Inc.) system at ultrahigh vacuum (1×10^{-9} bar) with a monochromated Al k_α X-ray source. The charge compensation was achieved with a combination of electron and argon ion flood guns. The X-ray beam size was 100 μm and survey spectra were recorded with pass energy (PE) of 117 eV, step size of 1 eV, and dwell time of 20 ms; whereas high-energy resolution spectra were recorded with PE of 47 eV, step size 0.1 eV, and dwell time of 20 ms. Auto-z (i.e., automated height adjustment to the highest intensity) was performed before each measurement to find the analyzer's focal point. The number of average sweeps of each element was adjusted to obtain the optimal signal-to-noise ratio.

Optical properties of $\text{Ti}_3\text{C}_2\text{T}_x$ and the hybrid photocatalysts were studied using a variety of spectroscopic techniques. UV-Visible (UV-Vis) spectra were obtained using a Shimadzu UV-2600 spectrometer. Photoluminescence (PL) spectroscopy was utilized to investigate electron-hole recombination in the hybrid photocatalysts. PL spectra were acquired via a spectraMax i3x multi-mode microplate reader over the range of 400–700 nm using an excitation wavelength of 360 nm. Electron paramagnetic resonance (EPR) spectroscopy was employed to detect the generation of $\bullet\text{OH}$ radicals on the hybrid photocatalysts using 5,5-dimethyl-1-pyrroline N-oxide (DMPO, Enzo Life Sciences, Plymouth Meeting, MI, USA) as a spin trap. In brief, an aliquot (950 μL) of photocatalyst aqueous dispersion (1 mg in 5 mL water) was mixed with 50 μL aqueous solution of DMPO to a final spin probe concentration of 100 μM . The mixture was exposed to UV-light for 5 minutes to generate $\bullet\text{OH}$ radicals, then sampled into borosilicate EPR tubes (100 μL) for subsequent analysis (SpinScanX,

ADANI, Minsk, Belarus). The formation of DMPO spin adducts was quantified by calculating the total area under the curve via double-integration of the characteristic EPR peaks using GRAMS/AI™ Spectroscopy Software (Thermo Scientific™, Version 9).

3.2.4 Photocatalytic Activity Evaluation

3.2.4.1 Liquid Phase

Photocatalytic activity of TiO₂ and the synthesized photocatalysts in liquid phase were evaluated by the degradation of MB in a batch reactor under UV light irradiation at room temperature and pH =7. In a typical experiment, an aqueous solution of MB (8 mL of 0.04 mg/mL) was placed in the batch reactor, and 4 mg of photocatalyst was added under constant stirring. In the dark, the mixture was stirred for 30 minutes to achieve adsorption and desorption equilibrium between the photocatalyst and MB. Thereafter, the stirring was continued under UV illumination and a small amount of the slurry was taken every 5 minutes and analyzed by UV-Vis spectroscopy. The illumination system consists of two 25 W UV lamps (Sylvania 21703) without reflectors and the main wavelength of the lamp is 356 nm. Prior to UV-Vis analysis, the photocatalyst was recovered by centrifugation; MB concentration was determined by recording the change in absorbance at 664 nm. Based on the experimental data, the photocatalytic degradation of MB was fitted to a pseudo first-order reaction (Equation 3.1):

$$\frac{c}{c_0} = e^{-kt} \quad (3.1)$$

where k is the apparent constant of reaction rate, c is the concentration of MB, and t is the reaction time.

3.2.4.2 Gas Phase

Photocatalytic activity of TiO₂ and synthesized photocatalysts in gas phase were evaluated by the oxidation of NO_x in a continuous flow reactor, described elsewhere [30, 31]. A substrate coated with a photocatalyst was loaded into the reactor and irradiated with UV light for 1 hour under

continuous airflow to remove adsorbed contaminants. Then, the light was turned off and the NO_x was introduced to the reactor for adequate adsorption of gaseous molecules on photocatalyst surface. The light was then turned on and the reaction was monitored at 1.0 ppm NO_x with a total airflow of 3000 sccm at a relative humidity of 50 %. After 2 hours of reaction, the light was turned off and NO_x was allowed to re-equilibrate. Concentrations of NO, NO₂, and NO_x were determined by averaging all data obtained during the oxidation reaction.

To evaluate the photocatalytic activity, DeNO_x index, an objective figure of merit for photocatalytic NO_x abatement, was utilized. DeNO_x index quantifies the net NO_x removal by considering NO conversion and product selectivity, defined as the percentage of NO completely oxidized to nitrates versus the total amount of NO oxidized to NO₂. To calculate the DeNO_x index, the photonic efficiency of NO, NO₂ and NO_x was first calculated using Equation 3.2 [32].

$$\xi = \frac{(c_d - c_i)\dot{V}p}{\phi ART} \quad (3.2)$$

where ξ is the photonic efficiency of a given specie; c_d is the species concentrations in dark; c_i is the species concentrations under illumination; $\dot{V}$ is the volumetric flow rate; p is the pressure in the system (1 atm); ϕ is the photon flux at photocatalyst surface (dependent of light wavelength and intensity); A is the catalyst irradiated area; R is the gas constant; T is the temperature.

The calculated photonic efficiency was then used to calculate the DeNO_x index and the selectivity by using Equations 3.3 and 3.4, respectively.

$$DeNO_x \text{ index} = \xi_{NO_x} \left(3 - \frac{2}{s} \right) \quad (3.3)$$

$$S = \frac{\xi_{NOx}}{\xi_{NO}} \quad (3.4)$$

3.3 Results and Discussion

3.3.1 Characterization of M-Ti₃C₂T_x and N-Ti₃C₂T_x

3.3.1.1 Morphology

From the SEM image of Ti₃AlC₂ in Figure 3.2a, the characteristic smooth surface of the MAX phase is apparent. After etching the MAX phase with LiF and HCl, the resulting exfoliated M-Ti₃C₂T_x (Figure 3.2b) exhibits the typical morphology of MXene produced by the so called "minimally intensive layer exfoliation" process [33]. Subsequent treatment with TPAOH yielded highly exfoliated MXene flakes as verified by the SEM image in Figure 3.2c, where the separated sheets can be easily observed. It is clear from the TEM images (Figures 3.2d and e) that the sheets of N-Ti₃C₂T_x are thinner and smaller than those of M-Ti₃C₂T_x. TEM-derived lateral dimensions of M-Ti₃C₂T_x and N-Ti₃C₂T_x were determined by averaging the length (longest distance) and width (shortest distance) of MXene sheets, following the approach reported by Xia et al. [34]. For both M-Ti₃C₂T_x and N-Ti₃C₂T_x, lateral dimensions of 106 sheets were first determined and the dimensions obtained are represented by distribution histograms (Figure 3.2g and h and Figure B3.1). Our analysis reveals that the average lateral dimensions of M-Ti₃C₂T_x and N-Ti₃C₂T_x are $1.34 \pm 0.5 \mu\text{m}$ and $181 \pm 86 \text{ nm}$, respectively. The HR-TEM image of N-Ti₃C₂T_x (Figure 3.2f) confirms the sheets are ultrathin, and the corresponding fast Fourier transform (FFT) reveals a highly crystalline structure. UV-Vis spectra of M-Ti₃C₂T_x and N-Ti₃C₂T_x dispersions in water (Figure 3.2i) reveal a transmittance of approximately 65% for N-Ti₃C₂T_x and 40% for M-Ti₃C₂T_x, indicating that N-Ti₃C₂T_x is more transparent than M-Ti₃C₂T_x. The strong absorption peak below 300 nm is attributed to the optical glass cuvette used in the measurement.

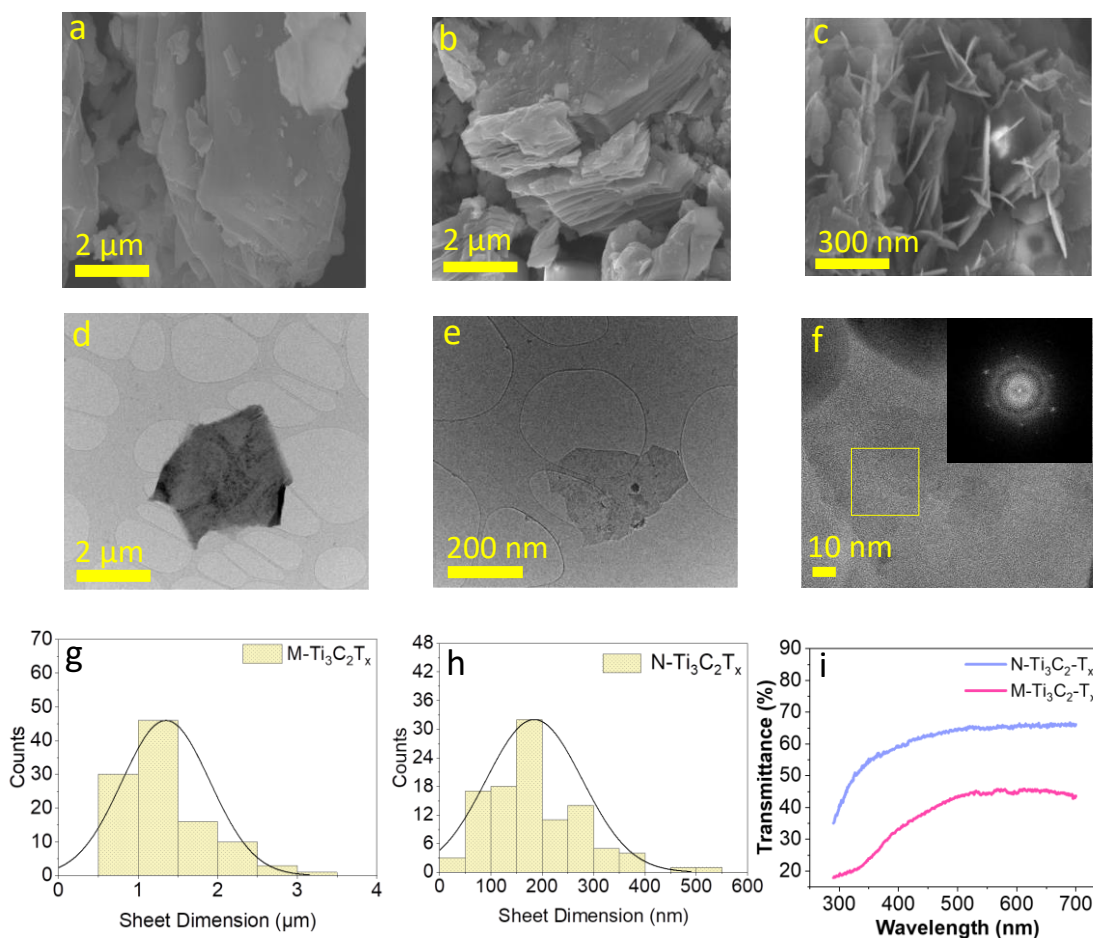


Figure 3.2 SEM images of Ti_3AlC_2 (a), $\text{M-Ti}_3\text{C}_2\text{T}_x$ (b), and $\text{N-Ti}_3\text{C}_2\text{T}_x$ (c). TEM images of $\text{M-Ti}_3\text{C}_2\text{T}_x$ (d) and $\text{N-Ti}_3\text{C}_2\text{T}_x$ (e). HR-TEM image of $\text{N-Ti}_3\text{C}_2\text{T}_x$ (f) and the FFT pattern corresponding to the yellow square in f (inset). Dimension distribution histograms of $\text{M-Ti}_3\text{C}_2\text{T}_x$ (g) and $\text{N-Ti}_3\text{C}_2\text{T}_x$ (h) from TEM images. UV-Vis spectra of $\text{M-Ti}_3\text{C}_2\text{T}_x$ and $\text{N-Ti}_3\text{C}_2\text{T}_x$ dispersions in water (i). Reproduced from reference [24]. Copyright Elsevier 2022.

Further structural characterization of the MXenes was carried out using XRD and Raman spectroscopy. XRD spectra of Ti_3AlC_2 , $\text{M-Ti}_3\text{C}_2\text{T}_x$, and $\text{N-Ti}_3\text{C}_2\text{T}_x$ are presented in Figure 3.3a. The peaks at $2\Theta = 9.5^\circ, 19.2^\circ, 34.0^\circ, 36.8^\circ, 39.0^\circ, 41.8^\circ, 44.9^\circ, 48.5^\circ, 52.4^\circ, 56.5^\circ$, and 60.3° are indexed to (002), (004), (101), (103), (104), (105), (106), (107), (108), (109), and (110) planes of Ti_3AlC_2 , respectively [35, 36]. The decrease in structural order and crystallinity are apparent after Al etching, as evidenced by the broadening of the diffraction peaks of $\text{M-Ti}_3\text{C}_2\text{T}_x$ and $\text{N-Ti}_3\text{C}_2\text{T}_x$. The (002) peak in $\text{M-Ti}_3\text{C}_2\text{T}_x$ shifts to lower angle ($2\Theta = 6.2^\circ$) than that of Ti_3AlC_2 , due to the increase in d -spacing, which is a consequence lattice expansion from Al removal and introduction of terminal functional groups. Interestingly, the shift in (002) peak is regarded as an indication of the successful exfoliation of MXene sheets [36]. The (002) peak in $\text{N-Ti}_3\text{C}_2\text{T}_x$ shifts to lower angle ($2\Theta = 5.5^\circ$) than that of $\text{M-Ti}_3\text{C}_2\text{T}_x$, indicating a change in surface terminal groups and the formation of highly exfoliated sheets after TPAOH treatment. In both $\text{M-Ti}_3\text{C}_2\text{T}_x$ and $\text{N-Ti}_3\text{C}_2\text{T}_x$, the peaks at 35.9 and 41.7 can be ascribed to TiC impurities, most likely formed during the fabrication process of Ti_3AlC_2 [37]. Raman spectra of Ti_3AlC_2 , $\text{M-Ti}_3\text{C}_2\text{T}_x$, and $\text{N-Ti}_3\text{C}_2\text{T}_x$ are shown in Figure 3.3b. The decrease in the intensities of peaks in the region between 200 and 700 cm^{-1} for $\text{M-Ti}_3\text{C}_2\text{T}_x$ and $\text{N-Ti}_3\text{C}_2\text{T}_x$ after Al etching is due to their structural deterioration and loss of crystallinity, which is consistent with the XRD results [1, 36, 38]. This phenomenon is accompanied by broadening of Raman peaks corresponding to the D-band ($\sim 1319\text{ cm}^{-1}$) and G-band ($\sim 1596\text{ cm}^{-1}$); these features are usually apparent after exfoliation of MXenes and generation of graphitic carbon and defects [39, 40].

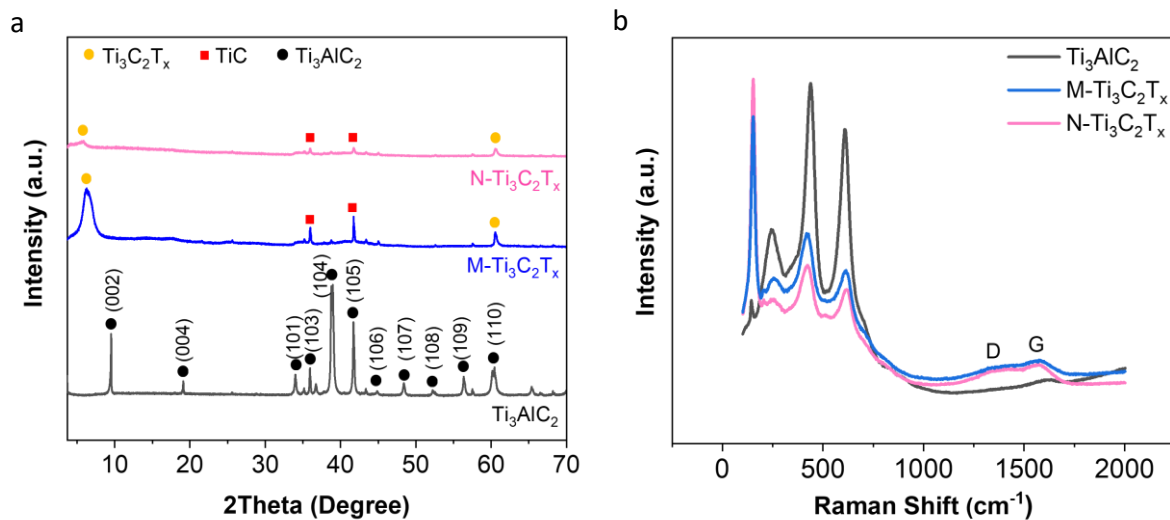


Figure 3.3 XRD spectra of Ti_3AlC_2 , $\text{M-Ti}_3\text{C}_2\text{T}_x$, and $\text{N-Ti}_3\text{C}_2\text{T}_x$ (a). Raman spectra of Ti_3AlC_2 , $\text{M-Ti}_3\text{C}_2\text{T}_x$, and $\text{N-Ti}_3\text{C}_2\text{T}_x$ (b). Reproduced from reference [24]. Copyright Elsevier 2022.

3.3.1.2 Surface Chemistry

To investigate the surface chemistry of $\text{Ti}_3\text{C}_2\text{T}_x$, high-resolution XPS analysis of Ti 2p and C 1s core levels was conducted for $\text{M-Ti}_3\text{C}_2\text{T}_x$ and $\text{N-Ti}_3\text{C}_2\text{T}_x$, and the results are shown in Figure 3.4. For $\text{M-Ti}_3\text{C}_2\text{T}_x$, the Ti 2p_{3/2} (2p_{1/2}) spectrum (Figure 3.4a) was deconvoluted into six peaks, corresponding to Ti-C, Ti(II), Ti(III), Ti(IV), $\text{TiO}_{2-x}\text{F}_x$, and Ti-F. The peak at 454.8 (460.8) eV is assigned to Ti-C and originates from the interior Ti atoms of $\text{M-Ti}_3\text{C}_2\text{T}_x$ [18, 41, 42]. The peaks at 456 (462), 457.6 (463.5), and 459 (464.8) eV correspond to Ti oxidation states and can be attributed to OH/O-Ti²⁺-C, OH/O-Ti³⁺-C, and TiO_2 , respectively [41, 42]. The peak 460 (466) eV is assigned to C-Ti-F [43]. The deconvolution of C 1s spectrum produces seven peaks (Figure 3.4b) at 281, 282.2, 284.4, 285, 285.6, and 288.7 eV and are attributed to C-Ti, C-Ti-T_x, C=C, C-C, C-O, and COO, respectively [41, 43-47]. XPS peak fitting shows the dominant terminals on $\text{M-Ti}_3\text{C}_2\text{T}_x$ surface are =O, -OH, and -F.

For N-Ti₃C₂T_x, the binding energies of Ti 2p peaks shift to lower values (Figure 3.4c), most likely due to the introduction of defects as a result of TPAOH treatment—a phenomenon that has been observed in transition metal carbides [43]. The Ti-C, (OH or O)-Ti²⁺-C, (OH or O)-Ti³⁺-C, TiO₂ and C-Ti-F_x are located at 453.5 (459.5), 454.9 (461), 456.6 (462.5), 457.7 (463.5), and 458.8 (464.8) eV [39, 43, 48]. In C 1s region (Figure 3.4d), the peaks corresponding to C-Ti, C-Ti-T_x, C=C, C-C, and C-O are located at 280.3, 282.7, 284, 285, and 286.6 eV, respectively. In comparison to M-Ti₃C₂T_x, the intensities of peaks corresponding to sp² C and sp³ C in N-Ti₃C₂T_x are higher, indicating an increase in the amounts of graphitic carbon and defects in N-Ti₃C₂T_x as observed in the Raman results.

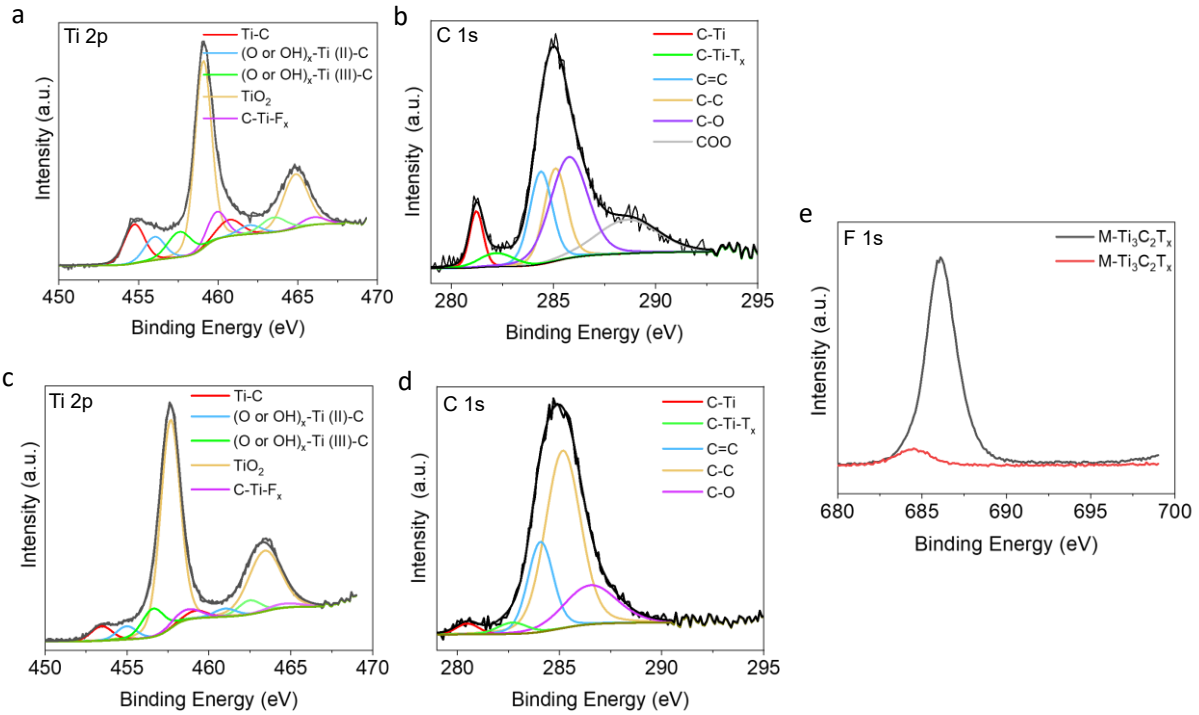


Figure 3.4 High-resolution XPS spectra of M-Ti₃C₂T_x in (a) Ti 2p and (b) C 1s. High-resolution XPS spectra of N-Ti₃C₂T_x in (c) Ti 2p and (d) C 1s. High-resolution XPS spectra of M-Ti₃C₂T_x and N-Ti₃C₂T_x in (e) F 1s. Reproduced from reference [24]. Copyright Elsevier 2022.

The high-resolution XPS spectra in F 1s region (Figure 3.4e) show the decrease in the intensity of F_x peak for N-Ti₃C₂T_x in comparison to that of M-Ti₃C₂T_x. We therefore conclude that TPAOH

treatment reduces the amount of fluorine on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$. The change in the terminal functional groups of $\text{M-Ti}_3\text{C}_2\text{T}_x$ upon TPAOH treatment was corroborated by FTIR analysis, evidenced by peaks corresponding to C-O, C=O, OH, and COOH exhibiting substantially higher intensities in $\text{N-Ti}_3\text{C}_2\text{T}_x$ than $\text{M-Ti}_3\text{C}_2\text{T}_x$ (Figure B3.2). It is worth mentioning that the adsorption of pollutants such as MB, CO_2 , and thiophene on $\text{Ti}_3\text{C}_2\text{T}_x$ surface is primarily controlled by -O and -OH functional groups [4, 21-23]. Hence, the role of TPAOH is not only beneficial in altering the morphology of MXene, but also in adapting the surface chemistry for enhanced pollutant adsorption.

3.3.2 Characterization of $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$ and $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ Photocatalysts

TEM was utilized to investigate the interfacial contact between $\text{Ti}_3\text{C}_2\text{T}_x$ and TiO_2 in $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$ and $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ hybrid photocatalysts. Figures 3.5a and b reveal the highly exfoliated and transparent $\text{N-Ti}_3\text{C}_2\text{T}_x$ is in direct contact with TiO_2 , and the high-magnification image (Figure 3.5c) reveals the intimate interaction between $\text{N-Ti}_3\text{C}_2\text{T}_x$ and TiO_2 . The strong interfacial contact between $\text{N-Ti}_3\text{C}_2\text{T}_x$ and TiO_2 undoubtedly improves the quality of the junction formed between them, and is expected to facilitate charge carrier mobility across the interface. On the other hand, even though $\text{M-Ti}_3\text{C}_2\text{T}_x$ is exfoliated, the sample is thicker than $\text{N-Ti}_3\text{C}_2\text{T}_x$, and the TiO_2 tends to aggregate on the edges of $\text{M-Ti}_3\text{C}_2\text{T}_x$ (Figures 3.5d and e). In addition, the high-magnification image in Figure 3.5f shows the poor interfacial contact between TiO_2 and $\text{M-Ti}_3\text{C}_2\text{T}_x$ — in fact, only a small fraction of TiO_2 is in direct contact with $\text{M-Ti}_3\text{C}_2\text{T}_x$ due to the low-quality junction formed between the two components. The charge carrier mobility across the interface in $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$ is therefore diminished in comparison to $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$.

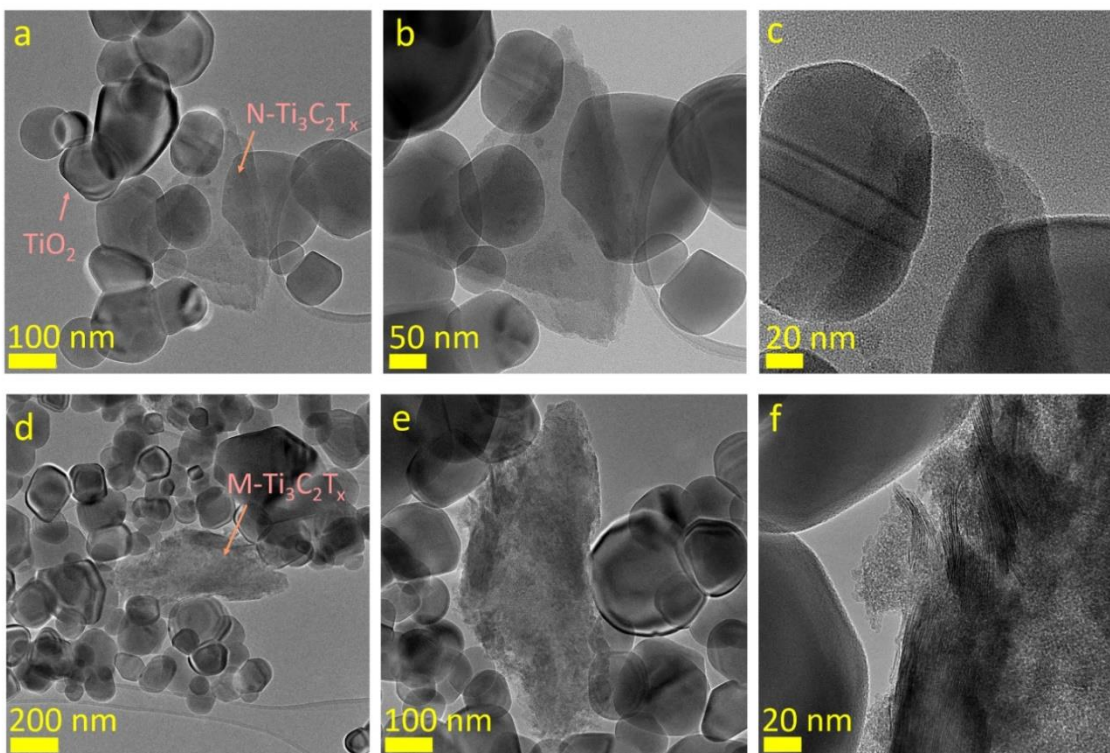


Figure 3.5 TEM images of $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ at different magnifications (a, b, and c). TEM images of $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$ at different magnifications (d, e, and f). Reproduced from reference [24]. Copyright Elsevier 2022.

XRD spectra of $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ and $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$ photocatalysts are shown in Figures B3.3 a and b, where the peaks ascribed to anatase TiO_2 are obvious and consistent with the literature [49, 50]. For $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$, the (002) peak of $\text{Ti}_3\text{C}_2\text{T}_x$ was not detected at low concentration of $\text{N-Ti}_3\text{C}_2\text{T}_x$, an observation that is consistent with our previous study whereby low amount of SWCNTs was coupled with TiO_2 to facilitate electron-hole separation [51]. However, the peak intensity increases with $\text{N-Ti}_3\text{C}_2\text{T}_x$ concentration. A similar trend was observed for $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$, whereby the (002) peak of $\text{Ti}_3\text{C}_2\text{T}_x$ becomes dominant at high concentration of $\text{M-Ti}_3\text{C}_2\text{T}_x$. No peak associated with Ti_3AlC_2 was detected in both photocatalysts and the position of (002) peak for $\text{N-Ti}_3\text{C}_2\text{T}_x$ is still located

at a lower angle than that of M-Ti₃C₂T_x as observed in Figure 3a, an indication that the highly exfoliated Ti₃C₂T_x did not restack after coupling with TiO₂.

The Raman spectra of the pristine TiO₂ and TiO₂ modified with different concentrations of N-Ti₃C₂T_x and M-Ti₃C₂T_x are shown in Figures B3.3c and d. The Raman spectra reveal the four characteristic peaks attributed to anatase vibration modes of TiO₂ [52, 53]. Because the amount of N-Ti₃C₂T_x and M-Ti₃C₂T_x in the hybrids is small compared to that of TiO₂, no peak corresponding to Ti₃C₂T_x is observed in the spectra of TiO₂-N-Ti₃C₂T_x and TiO₂-M-Ti₃C₂T_x. However, at high concentrations of N-Ti₃C₂T_x and M-Ti₃C₂T_x, the intensities of these dominant anatase vibrational modes dramatically decreased, indicating the existence of Ti₃C₂T_x in the photocatalysts.

3.3.3 Photocatalytic Activity of M-Ti₃C₂T_x and N-Ti₃C₂T_x in Liquid Phase

The photocatalytic activity of TiO₂-N-Ti₃C₂T_x and TiO₂-M-Ti₃C₂T_x in the degradation of MB (Figures 3.6a, b and c) is sensitive to the amount of Ti₃C₂T_x in the hybrid photocatalysts. Significant improvement in the photocatalytic activity of TiO₂ was achieved when the amounts of N-Ti₃C₂T_x and M-Ti₃C₂T_x in the hybrids were 30 wt% and 2.5 wt%, respectively; these compositions were considered as the optimum for the respective photocatalysts. The rate constant (*k*) for MB degradation using the optimized TiO₂-N-Ti₃C₂T_x photocatalyst with 30wt% N-Ti₃C₂T_x is 0.020 min⁻¹, which is over three times higher than that of TiO₂ (0.006 min⁻¹), and almost two times higher than that of optimized TiO₂-M-Ti₃C₂T_x with 2.5 wt% M-Ti₃C₂T_x (0.012 min⁻¹). Self-photosensitization of MB under UV light has been excluded as MB removal in absence of a photocatalyst is negligible (data not shown for the sake of brevity). Interestingly, TiO₂-N-Ti₃C₂T_x shows extremely high photocatalytic activity when compared to TiO₂-O-Ti₃C₂T_x as shown in Figures 3.7a and b. The nucleation of TiO₂ on Ti₃C₂T_x surface and subsequent generation of TiO₂-O-Ti₃C₂T_x by thermal oxidation was confirmed by TEM, FTIR, and PL analysis as shown in Figure B3.4. The rate constant obtained for the reaction with TiO₂-

N-Ti₃C₂T_x is 20 times higher than that of TiO₂-O-Ti₃C₂T_x ($k = 0.001 \text{ min}^{-1}$). Furthermore, TiO₂-N-Ti₃C₂T_x exhibited good stability in four consecutive MB degradation experiments (Figure B3.5).

Direct comparison of the activity of TiO₂-N-Ti₃C₂T_x with other state-of-the-art photocatalysts in the literature can be misleading without a good understanding of the photocatalytic reaction conditions. Therefore, for meaningful comparison with our work, photocatalyst concentration, light wavelength, MB concentration, and MB removal percentage from recent seminal studies are summarized in Table 3.1. It is clear that TiO₂-N-Ti₃C₂T_x exhibits superior performance to other state-of-the-art photocatalysts especially at relatively low photocatalyst amount.

Table 3.1 Comparison of the activity for removal of MB under UV light after 35 minutes using TiO₂- Ti₃C₂T_x hybrid photocatalysts and a variety of high-performance photocatalysts in the literature.

Catalyst	MB Concentration (mg/mL)	Catalyst Weight (mg)	MB removal (%)	Light Source	Reference
TiO ₂ -N-Ti ₃ C ₂ T _x	0.04	4 (0.5 mg/ml)	92	25 W UV lamp (356 nm)	This study
TiO ₂ -M-Ti ₃ C ₂ T _x	0.04	4 (0.5 mg/ml)	75	25 W UV lamp (356 nm)	This study
TiO ₂ -O-Ti ₃ C ₂ T _x	0.04	4 (0.5 mg/ml)	15	25 W UV lamp (356 nm)	This study
TiO ₂	0.04	0.5 mg/l	53	25 W UV lamp (356 nm)	This study
P25*	0.05	50	30	-	[54]
P25-graphene	0.01	30 (0.75 mg/ml)	70	100 W Hg lamp (365 nm)	[55]
P25-CNT**	0.01	30 (0.75 mg/ml)	60	100 W Hg lamp (365 nm)	[55]
Ag-TiO ₂	0.00639	-	50	500 W Xe lamp	[56]
Pt-TiO ₂ -CNT	$6.26 \times 10^{-5} \text{ M}$	2	55	200 W Hg lamp	[57]

Bamboo biochar/TiO ₂	0.0128	10	90	700 W Hg lamp	[58]
TiO ₂ -graphene (calcinated at 200 C)	0.0147	10 (0.05 mg/ml)	87	17 W lamp (360 nm)	[59]
SiO ₂ -TiO ₂	0.0125	180 (3 mg/ml)	80	10 W UV lamp	[60]
SnO-AC***	0.1	250 (0.5 mg/ml)	75	8 W UV lamp (254 nm)	[61]
NiO-AC	0.1	250 (0.5 mg/ml)	70	8 W UV lamp (254 nm)	[61]
WO ₃ -AC	0.1	250(0.5 mg/ml)	40	8 W UV lamp (254 nm)	[61]
TiO ₂ -AC	0.1	250 (0.5 mg/ml)	40	8 W UV lamp (254 nm)	[61]
C ₆₀ -TiO ₂	0.005	100 mg (0.4 mg/ml)	60	8 W UV-A lamp	[62]
Cellulose-GO- TiO ₂	0.01	Hydrogel film (120 -80-0.5 mm ³)	52	125 W Hg lamp (312 nm)	[63]
TiO ₂ rod	0.01	60 (0.2 mg/ml)	85	16 W UV lamp (254 nm)	[64]
Fe ₃ O ₄	0.07	40 (0.13 mg/ml)	20	UV light (250 nm)	[65]
Fe ₃ O ₄ -TiO ₂	0.07	40 (0.13 mg/ml)	25	UV light (250 nm)	[65]
Fe ₃ O ₄ -SiO ₂	0.07	40 (0.13 mg/ml)	50	UV light (250 nm)	[65]
TiO ₂ @C sheet	0.02	10 (0.2 mg/ml)	30	500 W Hg lamp	[66]

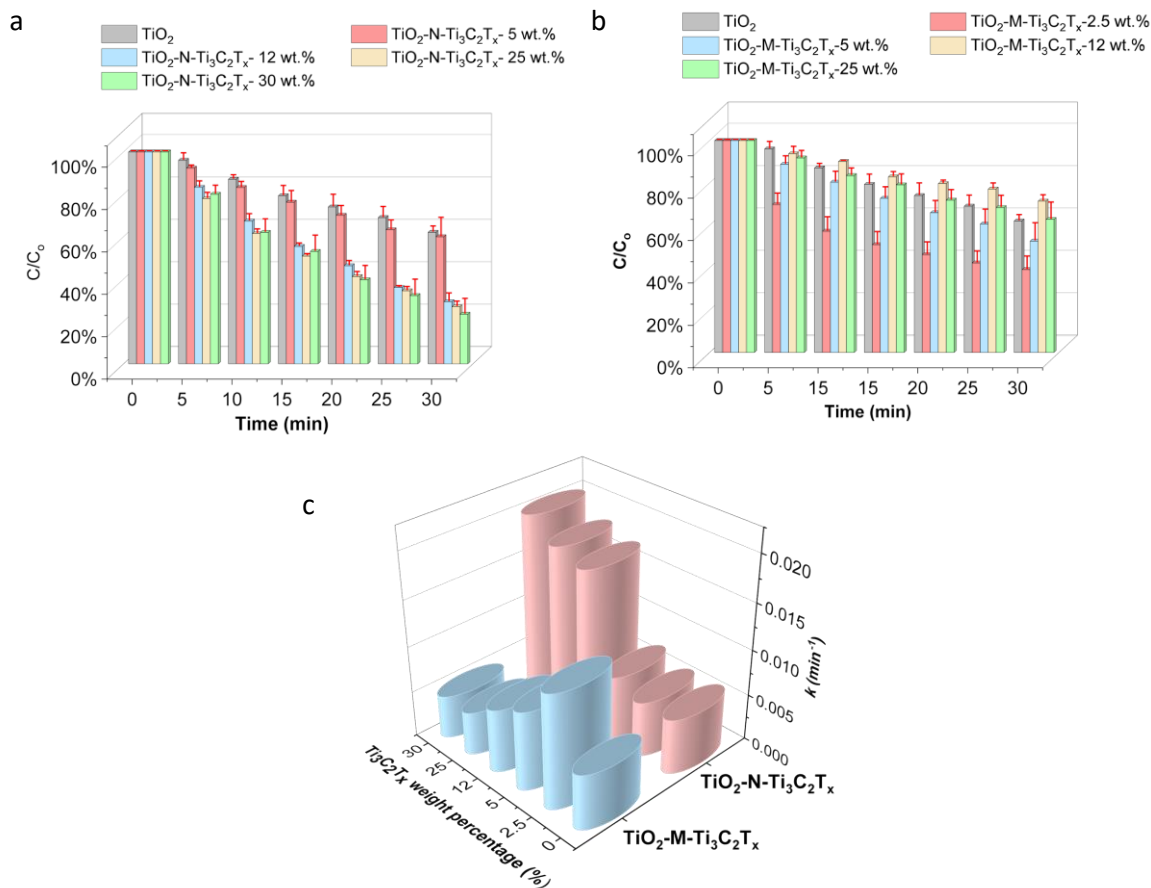


Figure 3.6 Photocatalytic degradation of MB using $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ (a) and $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$ (b) as a function of the amount of $\text{Ti}_3\text{C}_2\text{T}_x$ in the hybrids. Rate constant for MB photodegradation using $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ and $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$ as a function of the amount of $\text{Ti}_3\text{C}_2\text{T}_x$ in the hybrids (c). Reproduced from reference [24]. Copyright Elsevier 2022.

To rationalize the superior photocatalytic performance of $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$, we probed the PL emissions of TiO_2 , $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$, and $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$. Figure 3.8a shows the quenching in PL intensity after the addition of $\text{Ti}_3\text{C}_2\text{T}_x$, in which $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ shows the lowest intensity. Since PL emissions are generated from charge carrier recombination, a lower PL intensity indicates higher electron-hole separation [67]. The PL intensities reveal decreased electron-hole recombination was achieved in TiO_2 that is coupled with $\text{N-Ti}_3\text{C}_2\text{T}_x$, which we attribute to the intimate interfacial contact between them, as verified earlier by TEM (Figure 3.5c). The generation of $\bullet\text{OH}$ radicals on

photocatalyst surface, a key step in the photocatalytic degradation process, is generally attributed to the interaction between photogenerated holes and water molecules [68]. This claim is supported by our results in Figure B3. 6 that show poor MB degradation by $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ in the presence of a hole scavenger (ethanol). To investigate the generation of $\bullet\text{OH}$ radicals on TiO_2 and the hybrid photocatalysts, EPR spectroscopy with a DMPO spin trap approach was utilized. As shown in Figure 3.8b, the peaks detected in EPR spectra of TiO_2 , $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$, and $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ were negligible before light exposure.

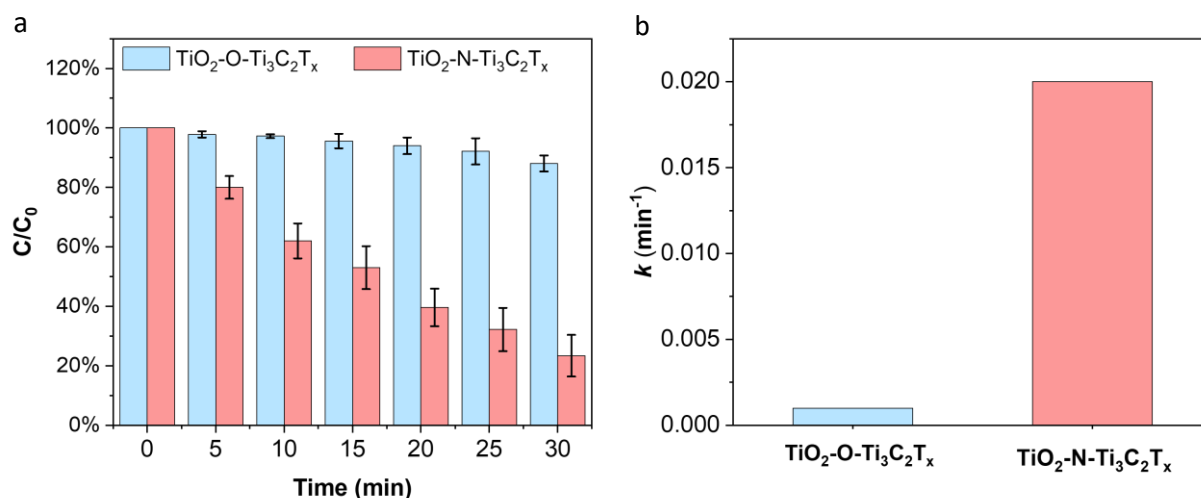


Figure 3.7 Photocatalytic degradation of MB (a) and the rate constant for MB photodegradation (b) by $\text{TiO}_2\text{-O-Ti}_3\text{C}_2\text{T}_x$ and $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$. Reproduced from reference [24]. Copyright Elsevier 2022.

Contrarily, after five minutes of light irradiation, the three photocatalysts show noticeable peaks which are attributed to the photogeneration of $\bullet\text{OH}$ radicals [2, 69]. The intensities of EPR peaks detected in the presence of $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ were greater than those of pristine TiO_2 and $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$; the areas under the characteristic DMPO quadruplet spectra of TiO_2 , $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$, and $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ were 230, 243.5, and 260 (a.u.), respectively. Based on EPR theory, the areas calculated via double-integration are proportional to the number of DMPO-hydroxyl radical spin

adducts [70], and therefore, higher values indicate higher concentration of $\bullet\text{OH}$ radicals on photocatalyst surface. The EPR analysis further confirms the effective electron-hole separation in $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ and the subsequent generation of $\bullet\text{OH}$ radicals. The efficient formation of OH radicals is also attributed to the high transparency of $\text{N-Ti}_3\text{C}_2\text{T}_x$, which ensures excellent photon- TiO_2 interaction during the photocatalytic reaction, as opposed to the thick $\text{M-Ti}_3\text{C}_2\text{T}_x$ with relatively lower transparency.

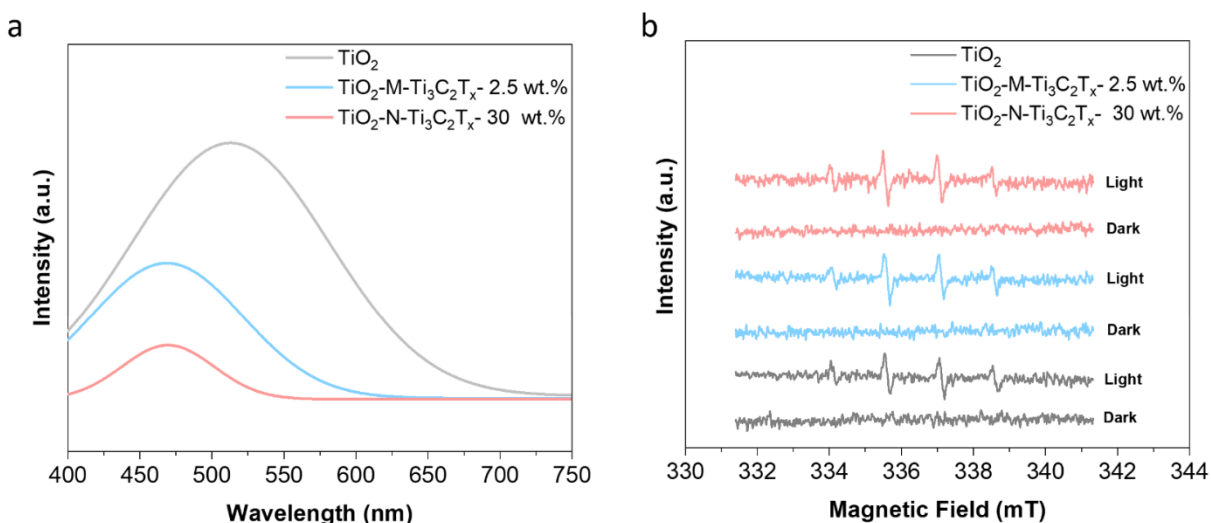


Figure 3.8 PL spectra of TiO_2 , $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$, and $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ (a) and EPR spectra of DMPO-hydroxyl radical spin adducts produced from TiO_2 , $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$, and $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ in aqueous dispersion (0.2 mg/mL) after 5 minutes of UV irradiation (b). Reproduced from reference [24]. Copyright Elsevier 2022.

Furthermore, it has been shown that the positively charged MB molecules can be easily adsorbed on the negatively charged terminals (particularly, on oxygen-containing terminals) of $\text{Ti}_3\text{C}_2\text{T}_x$, leading to their subsequent removal from water [21, 22]. Hence, it is reasonable to hypothesize that the abundant oxygen-containing terminals on $\text{N-Ti}_3\text{C}_2\text{T}_x$ are contributing to the superior degradation of MB achieved by $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$. To test the hypothesis, we reduced the number of sites available for MB adsorption through sodium ion-intercalation phenomenon. It has been shown that upon $\text{Ti}_3\text{C}_2\text{T}_x$ dispersion in NaOH aqueous solution, the negatively charged groups on the surface

are compensated by Na^+ [71]. The attachment of Na^+ to the negatively charged functional groups, which occurs most likely via ionic bonds, should reduce the available sites for MB adsorption and as a result hamper the non-photocatalytic route for MB removal. $\text{N-Ti}_3\text{C}_2\text{T}_x$ with Na^+ , designated as $\text{Na-Ti}_3\text{C}_2\text{T}_x$, was obtained after treatment with NaOH . $\text{Na-Ti}_3\text{C}_2\text{T}_x$ was then coupled with TiO_2 to produce a hybrid structure (designated as $\text{TiO}_2\text{-Na-Ti}_3\text{C}_2\text{T}_x$), which was also used in photocatalytic removal of MB. Results in Figure 3.9a and b show that MB removal by $\text{TiO}_2\text{-Na-Ti}_3\text{C}_2\text{T}_x$ is lower than that achieved by $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$. The reduction in catalyst activity upon using $\text{Na-Ti}_3\text{C}_2\text{T}_x$ as a cocatalyst instead of $\text{N-Ti}_3\text{C}_2\text{T}_x$ is attributed to the decrease of sites available for MB adsorption and the subsequent decrease in removal rate of MB by the non-photocatalytic route. It is important to highlight the following: (1) treating MXene with NaOH does not compromise its ability to separate the photogenerated charges [4]; and (2) although adsorption of MB on $\text{Na-Ti}_3\text{C}_2\text{T}_x$ can still occur via ion exchange between MB and Na^+ , previous investigations showed that the attachment of adsorbates on functional terminals of MXene is dominated by electrostatic interactions and hydrogen bonds [21, 22, 72]. We therefore conclude that the high photon- TiO_2 interaction and MB adsorption, as well as the reduced electron-hole recombination are responsible for the superior photocatalytic activity of $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$.

For liquid-phase reactions, solution pH is an important factor that should be considered as it impacts both photocatalyst surface charge and $\bullet\text{OH}$ radical generation. Hence, we conducted the degradation of MB in acidic and basic solutions using $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ photocatalyst (Figure 3.10a and b). In basic solution ($\text{pH} = 11$), the photocatalytic activity is significantly lower than that achieved at neutral environment ($\text{pH} = 7$). In the basic solution, the generation of $\bullet\text{OH}$ radicals is suppressed due to deprotonation of photocatalytic reaction intermediate on TiO_2 [73], and hence, the degradation rate of MB decreases. In addition, it has been suggested that increasing the basicity of solution (i.e. $\text{pH} > 8$) favors electron-hole recombination on photocatalyst surface [74], which could be another reason

for the observed reduction in the photocatalytic activity. In contrast, at pH = 2, the photocatalytic removal rate of MB decreased slightly compared to that at pH = 7. Since previous investigations imply that increasing the acidity of solution has no influence on active radical generation [74, 75], this slight reduction in the photocatalytic activity is attributed to the reduction in MB adsorption on N-Ti₃C₂T_x. In acidic solution, the negative zeta potential of N-Ti₃C₂T_x decreases and this consequently decreases the electrostatic interactions between the cationic MB and N-Ti₃C₂T_x surface [76], inhibiting the adsorption of MB on the photocatalyst surface and subsequent MB removal via the non-photocatalytic route.

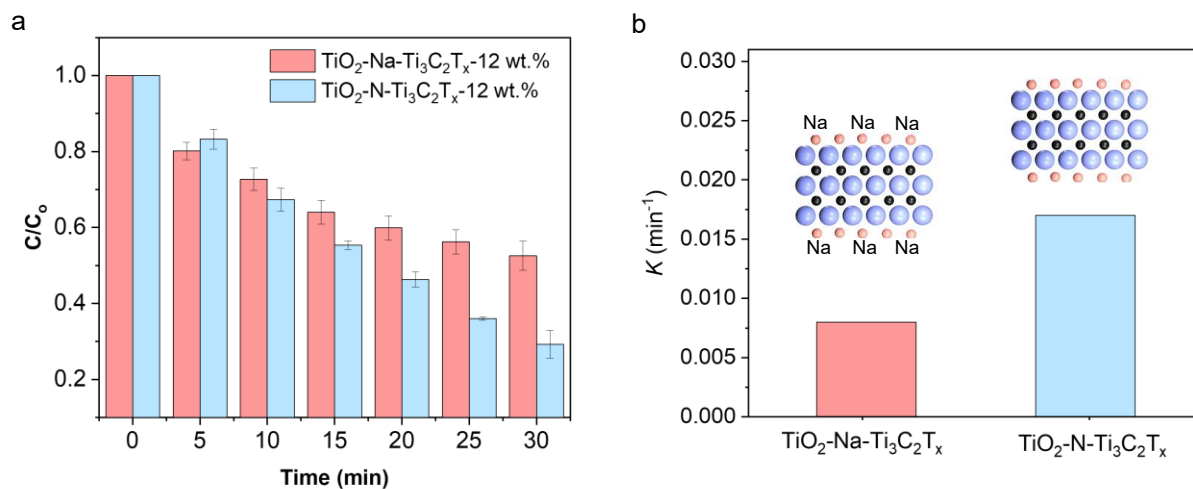


Figure 3.9 Photocatalytic degradation of MB using $\text{TiO}_2\text{-Na-Ti}_3\text{C}_2\text{T}_x$ and $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ (a). Rate constant for MB photodegradation by $\text{TiO}_2\text{-Na-Ti}_3\text{C}_2\text{T}_x$ and $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ (b). Reproduced from reference [24]. Copyright Elsevier 2022.

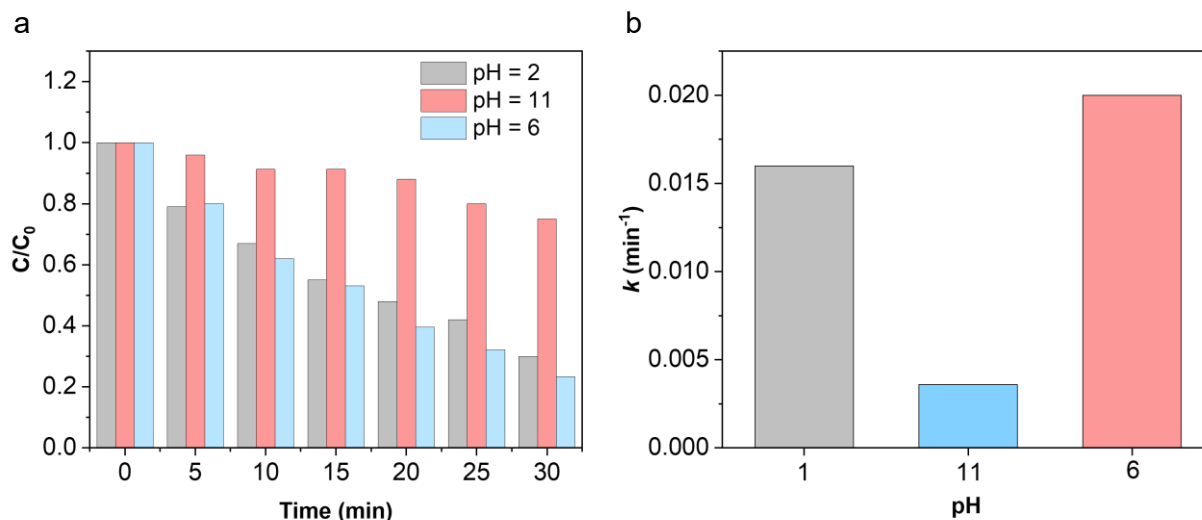


Figure 3.10 Photocatalytic degradation of MB (a) and the rate constant for MB photodegradation (b) by $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ at different pH. Reproduced from reference [24]. Copyright Elsevier 2022.

3.3.4. Photocatalytic Activity of $\text{M-Ti}_3\text{C}_2\text{T}_x$ and $\text{N-Ti}_3\text{C}_2\text{T}_x$ in Gas Phase

To demonstrate the versatility of $\text{N-Ti}_3\text{C}_2\text{T}_x$ as a cocatalyst in photocatalytic applications, we coupled $\text{N-Ti}_3\text{C}_2\text{T}_x$ with another form of TiO_2 (Degussa P25; a mixture of anatase and rutile) and the resulting hybrid (also designated as $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$) was used in the photocatalytic degradation of NO_x . The activity of $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ was evaluated by NO conversion and NO_x storage selectivity (Figure 3.11a) and DeNO_x index (Figure 3.11b), and compared to pristine TiO_2 and $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$ (fabricated by coupling P25 with $\text{M-Ti}_3\text{C}_2\text{T}_x$). TiO_2 exhibited reasonable NO conversion (53 %), but produced massive amount of NO_2 with low NO_x storage selectivity (58%) and negative DeNO_x index (-0.101), in agreement with previous reports [77-79]. In other words, TiO_2 oxidizes NO to NO_2 but fails to further oxidize NO_2 to other less toxic compounds such as nitrate and nitrite. Due to the high amount of NO_2 produced by TiO_2 and the higher toxicity of NO_2 than NO, it is apparent that TiO_2 is an ineffective photocatalyst for NO_x abatement. NO_x storage selectivity and DeNO_x index achieved by $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$ were 62 and -0.055, respectively, indicating the inadequacy of utilizing $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$ in photocatalytic NO_x oxidation. In contrast, $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ exhibited high NO_x abatement

performance, with very high NO_x storage selectivity (85%) and positive DeNO_x index (0.215) while maintaining the same NO conversion (55 %). The high photocatalytic NO_x removal achieved by $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ is attributed to the high photon- TiO_2 interaction and the reduced electron-hole recombination in $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$. It is noteworthy that recent studies dealing with gas sensor fabrication suggested that NO_x adsorbs effectively on oxygen-containing groups of MXene, where it can be stored in the form of other less toxic compounds (i.e. nitrate) [80, 81]. Hence, it is reasonable to hypothesize that the abundant oxygen-containing groups available on $\text{N-Ti}_3\text{C}_2\text{T}_x$ provide adsorption sites for NO_x in $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$, enabling the removal of NO_x through a non-photocatalytic route as well.

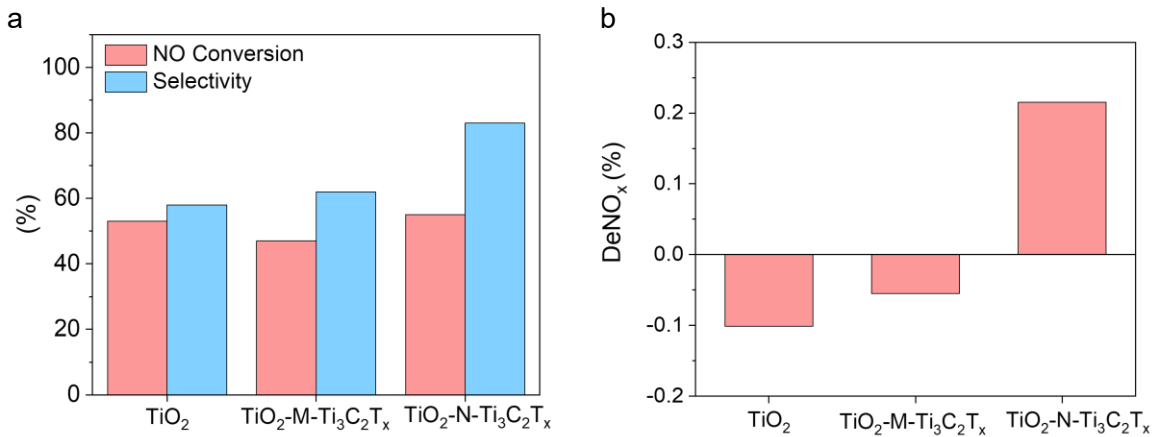


Figure 3.11 NO conversion and NO_x storage selectivity (a) and DeNO_x index (b) for TiO_2 , $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$, and $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$. Reproduced from reference [24]. Copyright Elsevier 2022.

3.3.5 Charge Carrier Dynamic in $\text{M-Ti}_3\text{C}_2\text{T}_x$ and $\text{N-Ti}_3\text{C}_2\text{T}_x$

A schematic illustration of charge carrier dynamic in $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ and $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$ and the subsequent removal of MB and NO_x are illustrated in Figure 3.12a and b. It is well known the conduction band (CB) and valence band (VB) of TiO_2 are located at -0.29 and 2.91 eV (vs. normal hydrogen electrode), respectively. For Ti_3AlC_2 , the valence state which is located below the Fermi level is split into two sub-bands: (1) Ti 3d-Al 3p orbitals (Band I) and (2) the hybridized Ti 3d-Al 3s

and Ti 3d-C 2p orbitals (Band II). After Al etching from Ti_3AlC_2 and the formation of $\text{Ti}_3\text{C}_2\text{T}_x$, Band II is dominated by Ti 3d and C 2p orbitals, and linked to Band I. Therefore, the weaker Ti-O coupling in energy state II results in the metallic phase of $\text{Ti}_3\text{C}_2\text{T}_x$ [2].

$\text{Ti}_3\text{C}_2\text{T}_x$ has a Fermi level of -0.04 eV with high density of free carriers ($8 \pm 3 \times 10^{21} \text{ cm}^{-3}$) and electrical conductivity ($4600 \pm 1100 \text{ S cm}^{-1}$). Consequently, the energy level of TiO_2 CB is more negative than the Fermi level of $\text{Ti}_3\text{C}_2\text{T}_x$, making it possible for photoexcited electrons to travel from TiO_2 CB to $\text{Ti}_3\text{C}_2\text{T}_x$, leaving holes in TiO_2 VB. In contrast to $\text{TiO}_2\text{-M-Ti}_3\text{C}_2\text{T}_x$, the concentration of electron-hole pairs is high in $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ due to the high transparency of $\text{N-Ti}_3\text{C}_2\text{T}_x$ and the intimate interfacial contact between TiO_2 and $\text{N-Ti}_3\text{C}_2\text{T}_x$. Electrons and holes react with oxygen and water molecules, respectively, to form $\bullet\text{OH}$ radicals (most active ROS in MB and NO_x degradation) and $\bullet\text{O}_2^-$ radicals that are also capable of degrading MB and NO_x pollutants. This phenomenon is robust in $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ due to the high concentration of charge carriers. Also, the abundant oxygen-containing terminals on $\text{N-Ti}_3\text{C}_2\text{T}_x$ in $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ can act as adsorption sites to facilitate the non-photocatalytic removal of MB and NO_x .

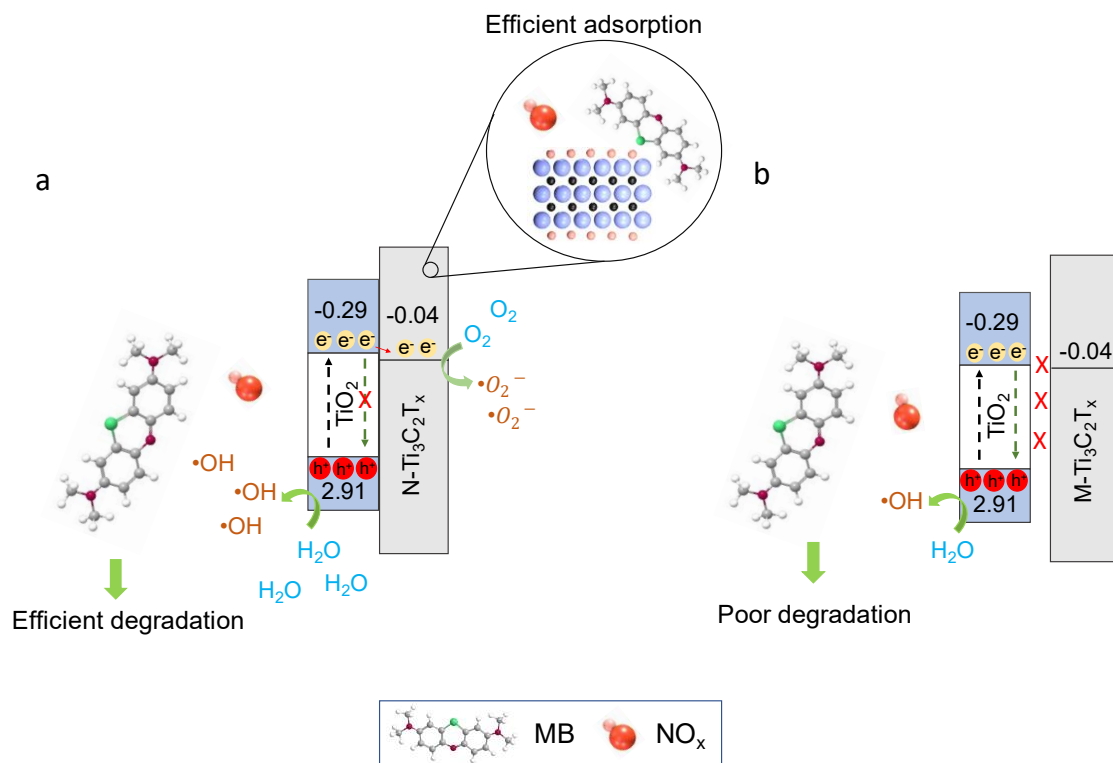


Figure 3.12 Schematic illustration of charge carrier dynamic and removal of MB and NO_x on TiO₂-N-Ti₃C₂T_x (a) and TiO₂-M-Ti₃C₂T_x (b) hybrid photocatalysts. Reproduced from reference [24]. Copyright Elsevier 2022.

3.3.6 Conclusions

We have successfully fabricated N-Ti₃C₂T_x with high transparency and abundant =O and -OH terminals using TPAOH as an exfoliating and fluorine-reducing agent. Coupling TiO₂ and N-Ti₃C₂T_x results in a hybrid photocatalyst with unique morphology and surface chemistry, as well as outstanding photocatalytic activity. The photocatalytic activity achieved by TiO₂-N-Ti₃C₂T_x in liquid phase and gas phase reactions is superior to that of other well-known TiO₂-Ti₃C₂T_x hybrids. Results showed that due to its small size and high transparency, N-Ti₃C₂T_x exhibits intimate interfacial contact with TiO₂ that enables effective electron-hole separation without interrupting photon flux to TiO₂. In addition, the unique surface chemistry of N-Ti₃C₂T_x facilitates efficient pollutant adsorption. Our findings show that N-Ti₃C₂T_x is a promising and high-performance cocatalyst with TiO₂. Therefore, the utilization of N-

Ti₃C₂T_x as an alternative cocatalyst to conventional Ti₃C₂T_x would enable the outstanding properties of MXenes to be fully exploited in photocatalysis.

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Chapter 4 - One-Step Synthesis of Delaminated, OH-Terminated Ti_3C_2 : High Photocatalytic NO_x Storage Selectivity Enabled by Coupling TiO_2 and $\text{Ti}_3\text{C}_2\text{-OH}$

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4.1 Introduction

MXenes, first fabricated at Drexel University by selective elimination of an A element (belong to group IIIA or IVA of the periodic table) from MAX phase, are 2D layered ternary materials with the general formula of M_{n+1}X_n (M = transition metal; X = carbon or nitrogen; and $n = 1, 2$, or 3) [1, 2]. Elimination of the A element in MAX phase results in a multi-layered structure that is terminated by functional groups (such as $=\text{O}$, $-\text{OH}$ and/or $-\text{F}$) and stabilized via van der Waals or hydrogen bonds, which is then delaminated into thin sheets by chemical intercalation with large-size organic molecules [3]. Generally, single- or few-layer MXene sheets offer an appealing combination of high ionic mobility, electrical conductivity, and chemical stability, as well as tunable structure and surface chemistry that are desired in many important applications [4, 5]. Even though the two-step etching-delamination process produces single- or few-layer 2D-MXene sheets, it requires high production cost and environmentally harmful when fluorine-containing compounds are involved [1-3]. Therefore, a one-step etching-delamination approach that is free of fluorine is needed.

Recent studies have highlighted the impact of functional groups attached to the planar Ti_3C_2 surface on its physical properties and performance in catalytic applications. For instance, the

adsorption of NO_2 is favored on Ti_3C_2 , particularly on OH-terminated Ti_3C_2 in the form of nitrites — a phenomenon that has been utilized to design effective NO_2 sensors [6-8]. Also, theoretical studies [9, 10] revealed the Fermi level of Ti_3C_2 strongly relies on its surface terminal groups. In particular, OH-terminated Ti_3C_2 has been shown to have an ultralow work function (1.6-2.8 eV), which can serve as a hole reservoir when coupled with TiO_2 facilitating electron-hole separation and subsequent photocatalytic activity [11-13]. Therefore, the surface chemistry of Ti_3C_2 can be tuned to suit the desired application. Nevertheless, utilization of Ti_3C_2 in photocatalytic air purification has been limited due to the lack of a rational framework for harnessing its properties in the design of photocatalysts.

Photocatalysis is an attractive approach for practical oxidation of NO_x (one of the criteria air pollutants according to the U.S. Environmental Protection Agency (EPA)) due to its strong ability to oxidize NO_x under ambient conditions and at relatively low concentrations. Photocatalytic NO_x oxidation can potentially serve as an alternative to traditional NO_x abatement approaches especially for NO_x pollution at part-per-billion (ppb) levels and in the presence of other pollutants (e.g., VOCs, SO_x , etc.) [14]. In addition, a hybrid approach that combines photocatalysis and a traditional approach (adsorption, plasma, or reduction) could lead to efficient removal of high levels of NO_x from industrial waste streams (flue gas). Although TiO_2 (P25, Degussa) is the gold standard photocatalyst under UV light, it possesses low selectivity towards NO_x storage in solid state and tends to convert NO to NO_2 , a considerably more toxic form of NO_x , especially at humid environment [15]. In other words, TiO_2 oxidizes NO to NO_2 but fails to store the produced NO_2 on catalyst surface in the forms of other non-volatile and less toxic compounds such as HNO_3 , NO_3^- , or NO_2^- . The low NO_x storage selectivity has limited the practical application of TiO_2 in NO_x abatement. To improve the activity of TiO_2 in NO_x oxidation, two broad strategies

classified as photocatalytic and non-photocatalytic have been explored. Photocatalytic processes involve enhancing electron-hole separation through coupling TiO_2 with nanocarbon (i.e. graphene) or creating defects in TiO_2 lattice to facilitate the generation of reactive oxygen species (ROS) and storage of NO_2 on catalyst surface in the form of HNO_3 [16, 17]. Non-photocatalytic processes involve coupling TiO_2 with non-photocatalytic nanostructures that can provide NO_x storage (adsorption) sites to store NO_2 on the catalyst surface in the form of NO_3^- or NO_2^- [18, 19]. Thus, due to its high affinity towards NO_2 adsorption and its ultralow work function, OH-terminated Ti_3C_2 appears to be well suited for coupling with TiO_2 to reduce charge carrier recombination and provide non-photocatalytic adsorption sites for NO_x storage, and thereby, effectively removes NO_x .

Herein, delaminated, OH-terminated Ti_3C_2 (designated as $\text{Ti}_3\text{C}_2\text{-OH}$) was fabricated in a single step and successfully coupled with commercial TiO_2 (P25, Degussa) to form a hybrid photocatalyst. Fabrication of $\text{Ti}_3\text{C}_2\text{-OH}$ was achieved using NaOH (etchant) and hydrazine (delaminating agent) to simultaneously extract Al from Ti_3AlC_2 and delaminate the sheets. Unique features of the one-step process are that it utilizes hydrazine-derived intercalants as alternatives to traditional liquid intercalants in a separate step, and it does not require the use of fluorine-containing etchants. Coupling TiO_2 and $\text{Ti}_3\text{C}_2\text{-OH}$ results in a strong synergistic effect that promotes photocatalytic abatement of NO_x .

4.2 Experimental

4.2.1 One-Step Etching and Delamination of Ti_3AlC_2

1 mmol of Ti_3AlC_2 (Carbon, Ukraine; particle size: 40 μm) was dispersed in 120 mL distilled water and 15 mL 70% hydrazine (Sigma-Aldrich, USA) was slowly added to it. Then, 0.12 mol of NaOH (Sigma-Aldrich, USA) as the etching agent was dissolved in the above solution.

The solution was transferred to a 200 mL Teflon lined hydrothermal autoclave and placed in an electric oven at 180 °C for 24 hours. After cooling the reactor to room temperature, the sample was collected by vacuum filtration aided by water and methanol. The collected sample was dried at room temperature and designated as E-Ti₃AlC₂.

4.2.2 Two-Step Etching and Delamination of Ti₃AlC₂

1 mmol of Ti₃AlC₂ was dispersed in 135 mL distilled water. Then, 0.12 mol of NaOH as the etching agent was dissolved in the above solution. The solution was transferred to a 200 mL Teflon lined hydrothermal autoclave and placed in an electric oven at 180 °C for 24 hours. After cooling the reactor to room temperature, the sample was collected by vacuum filtration aided by water and methanol. A section (130 mg) of the produced structure was delaminated in 10 mL hydrazine under stirring at room temperature for 24 hours. The final product was collected by vacuum filtration aided by water and methanol. The collected sample was dried at room temperature and designated as E-Ti₃AlC₂-2.

4.2.3 Etching of Ti₃AlC₂ by Conventional LiF/HCl Solution

1 g of LiF (Sigma-Aldrich, USA) was added to a Teflon container contains 10 mL 9 M HCl (Sigma-Aldrich, USA), and a magnetic stirrer was placed inside. 1 gram of Ti₃AlC₂ was slowly mixed with the solution. After adding the Ti₃AlC₂, the solution was maintained at 40 °C under stirred (300 rpm) for 36 hours. A Teflon lid was gently placed on the Teflon container. The final product was collected by vacuum filtration aided by water and methanol. The collected sample was dried at room temperature and designated as LiF-Ti₃AlC₂.

4.2.4 Synthesis of TiO₂-Ti₃C₂-OH and TiO₂-Ti₃C₂-F Photocatalysts

137 mg of E-Ti₃AlC₂ was dispersed in 30 mL distilled water by ultrasonication for 60 minutes. The dispersion was split into two parts and centrifuged at 4000 rpm for 15 minutes. The

supernatant containing $\text{Ti}_3\text{C}_2\text{-OH}$ was dropped slowly into the TiO_2 dispersion (2 g of P25 in 100 mL distilled water) under stirring, and the stirring was continued for 4 hours. Thereafter, $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ was collected by centrifugation and dried in air. For TiO_2 coupled with F-terminated Ti_3C_2 , the above procedure was followed, except that $\text{LiF-Ti}_3\text{AlC}_2$ was used; the resulting hybrid photocatalyst is designated as $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-F}$.

4.2.5 Synthesis of Conventional TiO_2 -Based Photocatalysts

Anatase TiO_2 (100 nm) was purchased from (US Research Nanotechnology, Inc) and used without modification. TiO_2 nucleation on OH-terminated Ti_3C_2 and F-terminated Ti_3C_2 was achieved by thermal treatment following the process reported by Li et al[20] and designated as $\text{Ti}_3\text{C}_2\text{-OH-400}$ and $\text{Ti}_3\text{C}_2\text{-F-400}$, respectively. Briefly, 300 mg of $\text{LiF-Ti}_3\text{AlC}_2$ or alkali-treated $\text{LiF-Ti}_3\text{AlC}_2$ was placed in tube furnace and calcined in air at 400 °C for 4 hours. The final products were stored in air until next use. For TiO_2 -graphene hybrid, graphene synthesised by catalyst-free gas phase hydrocarbon detonation process[21] using O_2 and C_2H_2 as precursors was received from Sorensen's group. 137 mg of the as-received graphene was dispersed in 30 mL distilled water by ultrasonication for 1 hour. Then, the dispersion was slowly dropped into TiO_2 dispersion (2 g of P25 in 100 mL distilled water) under stirring and kept under stirring for 4 hours. Thereafter, TiO_2 -graphene was collected by centrifugation and dried in air. TiO_2 impregnated with Ni was fabricated by a photo-deposition approach using a mixture of NiCl_2 and ethanol. Two different solutions were first prepared. Solution A composed of 2 mg of NiCl_2 dispersed in 20 mL distilled water while solution B composed of 2 g of TiO_2 (P25) dispersed in 5 mL ethanol. Solution B was slowly dropped into solution A under stirring and the pH of the mixture was adjusted to 8 using 0.1 M NaOH aqueous solution. The mixture was irradiated with UV light for 3 hours. The final product (designated as $\text{TiO}_2\text{-Ni}$) was collected by centrifugation and dried in air.

4.2.6 Photocatalyst Performance Evaluation

4.2.6.1 Substrate Preparation

The prepared photocatalysts were sieved to $<125\ \mu\text{m}$ and dispersed in ethanol at a ratio of 0.15g/ml via ultrasonication for 15 minutes. Each of the dispersions was poured onto a glass slide ($50 \times 100\ \text{mm}$) and cast with a doctor blade to $250\ \mu\text{m}$. The slides were allowed to dry and then used in the photocatalytic reaction.

4.2.6.2 Reactor Configuration

The photocatalytic experiment was conducted at room temperature in a continuous-flow reactor built in accordance with ISO standards except the use of a lower headspace distance (3 mm) based on the finding of our previous study [15]. The reactor was connected to two gas cylinders containing 100 ppm NO in N_2 and breathing air as shown in Figure C4.1. Mass flow controllers were used to monitor the flow rate of gases to the reactor. Sensor-push HT1 humidity sensor was utilized to measure the humidity inside the reactor. The reaction chamber was constructed from steel with a quartz glass window allowing UV light penetration to photocatalyst surface; the light intensity and wavelength were $2\ \text{mW}/\text{cm}^2$ and 320 nm, respectively. NO and NO_x concentrations were measured by Chemiluminescent 42C Low Source analyzer (Thermo Fisher Scientific).

4.2.6.3 Activity Measurement

To further examine the photocatalytic activity, De NO_x index, an objective figure of merit for photocatalytic NO_x abatement, was utilized. The De NO_x index is a measure of photonic efficiency during NO_x photocatalytic oxidation; it was proposed as a parameter to quantify the net NO_x removal by considering NO conversion as well as product selectivity, defined as the percentage of NO completely oxidized to nitrates versus the total amount of NO oxidized to NO_2 .

To calculate DeNO_x index, the photonic efficiency of NO, NO₂ and NO_x was first calculated using Equation 4.1 [22].

$$\xi = \frac{(c_d - c_i)\dot{V}p}{\varphi ART} \quad (4.1)$$

where ξ is the photonic efficiency of a given specie; c_d is the species concentrations in dark; c_i is the species concentrations under illumination; $\dot{V}$ is the volumetric flow rate; p is the pressure in the system (1 atm); φ is the photon flux at photocatalyst surface (dependent on light wavelength and intensity); A is the photocatalyst irradiated area; R is the gas constant; and T is the temperature. The calculated photonic efficiency was then used to calculate the DeNO_x index and the selectivity using Equations 4.2 and 4.3, respectively.

$$DeNO_x = \xi_{NO_x} \left(3 - \frac{2}{S} \right) \quad (4.2)$$

$$S = \frac{\xi_{NO_x}}{\xi_{NO}} \quad (4.3)$$

4.3 Results and Discussion

To extract Al from Ti₃AlC₂ by alkali treatment, an elevated temperature is needed [23, 24]. Therefore, Ti₃AlC₂ was immersed in a hydrothermal reactor containing aqueous solution of NaOH and hydrazine, and the reaction was conducted at 180 °C for 24 hours. At this temperature, phase transition of hydrazine from liquid to gas occurs, and generates gaseous molecules (N₂, H₂, and NH₃[25]); it is probable that NH₃ forms an equilibrium between gas and liquid states under the reaction conditions facilitating simultaneous etching and delamination. In this one-step process, the surface Al atoms gradually oxidize and the compounds formed dissociate in water by OH attack to form $Al(OH)_4^-$ while the generated NH_4^+ ions replace Al atoms and prevent Ti-layer

stabilization, producing $\text{Ti}_3\text{C}_2\text{-OH}$ that can be collected by centrifugation, as depicted in Figure 4.1.

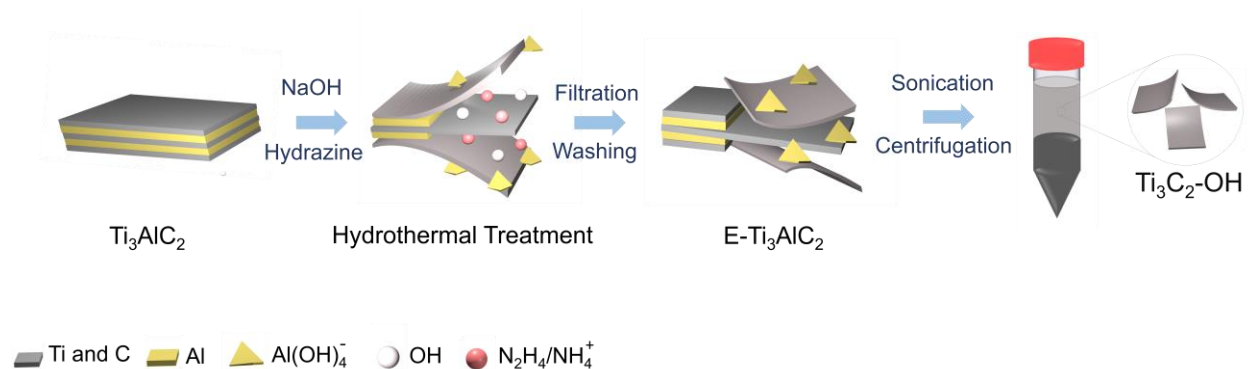


Figure 4.1 Schematic illustration of the one-step synthesis of $\text{Ti}_3\text{C}_2\text{-OH}$ involving hydrazine decomposition during alkali treatment. Reproduced from reference [46]. Copyright Elsevier 2022.

The morphology of Ti_3AlC_2 and $\text{E-Ti}_3\text{AlC}_2$ was characterized by scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS), and transmission electron microscopy (TEM). The SEM image of Ti_3AlC_2 (Figure 4.2a) shows the typical layered structure of MAX phase, where the layers are connected. After the hydrothermal treatment and Al etching, the connected layers were separated and thin $\text{Ti}_3\text{C}_2\text{-OH}$ sheets were generated. The SEM images of $\text{E-Ti}_3\text{AlC}_2$ (Figure 4.2b and Figure C4.2) show the generation of $\text{Ti}_3\text{C}_2\text{-OH}$ sheets on the surface of Ti_3AlC_2 which were then collected by sonication and centrifugation and subsequently drop cast on a Gilder imaging grid. The SEM image of collected $\text{Ti}_3\text{C}_2\text{-OH}$ shows that the sheets are thin and have lateral size of approximately one micrometer (Figure 4.2c). A TEM image of collected $\text{Ti}_3\text{C}_2\text{-OH}$ (Figure 4.2d) confirms the generation of thin and transparent sheets that are either single- or few-layer sheets (indicated by yellow arrows); this observation is further supported by high-magnification TEM image (Figure 4.2e) and a zoom-in TEM image (Figure 4.2f) that show a two-layer thick $\text{Ti}_3\text{C}_2\text{-OH}$ sheet with a monolayer thickness of ~ 1 nm. Our TEM analysis also reveals the presence of one-layer thick $\text{Ti}_3\text{C}_2\text{-OH}$ sheets (Figure C4.3a and b).

Elemental composition data from EDS reveal that Ti, C, and O were homogeneously distributed over the delaminated $\text{Ti}_3\text{C}_2\text{-OH}$ sheet with low Al content (Figure 4.2h), indicating the successful removal of a large fraction of Al.

X-ray diffraction (XRD) patterns of Ti_3AlC_2 and E- Ti_3AlC_2 are presented in Figure 4.3a. Both Ti_3AlC_2 and E- Ti_3AlC_2 show almost similar XRD patterns, and the characteristic diffraction peaks corresponding to crystal planes inherited from the Ti_3AlC_2 are obvious in E- Ti_3AlC_2 , consistent with other studies in which alkali was used as etchant to remove Al atoms [24, 26]. The slight reduction in the intensity of the peak corresponding to (002) plane (clearly shown in the zoom-in XRD patterns, Figure C4.4) and the disappearance of peaks indicated by green arrows in Figure 4.3a suggest the destruction of the ordered crystal structure of Ti_3AlC_2 after the etching process, due to the removal of surface Al atoms [26]. The Raman spectra of Ti_3AlC_2 and E- Ti_3AlC_2 are shown in Figure 4.3b. The characteristic peaks at 116, 145 and 260 cm^{-1} (labeled as 1, 2 and 3, respectively), attributed to the vibration of Ti and Al in Ti_3AlC_2 , vanished after the one-step process due to structure deterioration as a result of Al removal [27-29]. The peaks at 399 and 610 cm^{-1} (labeled 4 and 5, respectively), attributed to the vibration of C and Ti in Ti_3C_2 , broadened after the one-step process due to functional group attachment [29, 30]; the broad Raman peaks at 399 and 610 cm^{-1} are attributed to OH-terminated Ti_3C_2 [30, 31]. The broad G- and D-bands of E- Ti_3AlC_2 at 1350 and 1580 cm^{-1} in Figure C4.5 indicates the presence of free carbons in the sample and corroborates the removal of Al [32, 33].

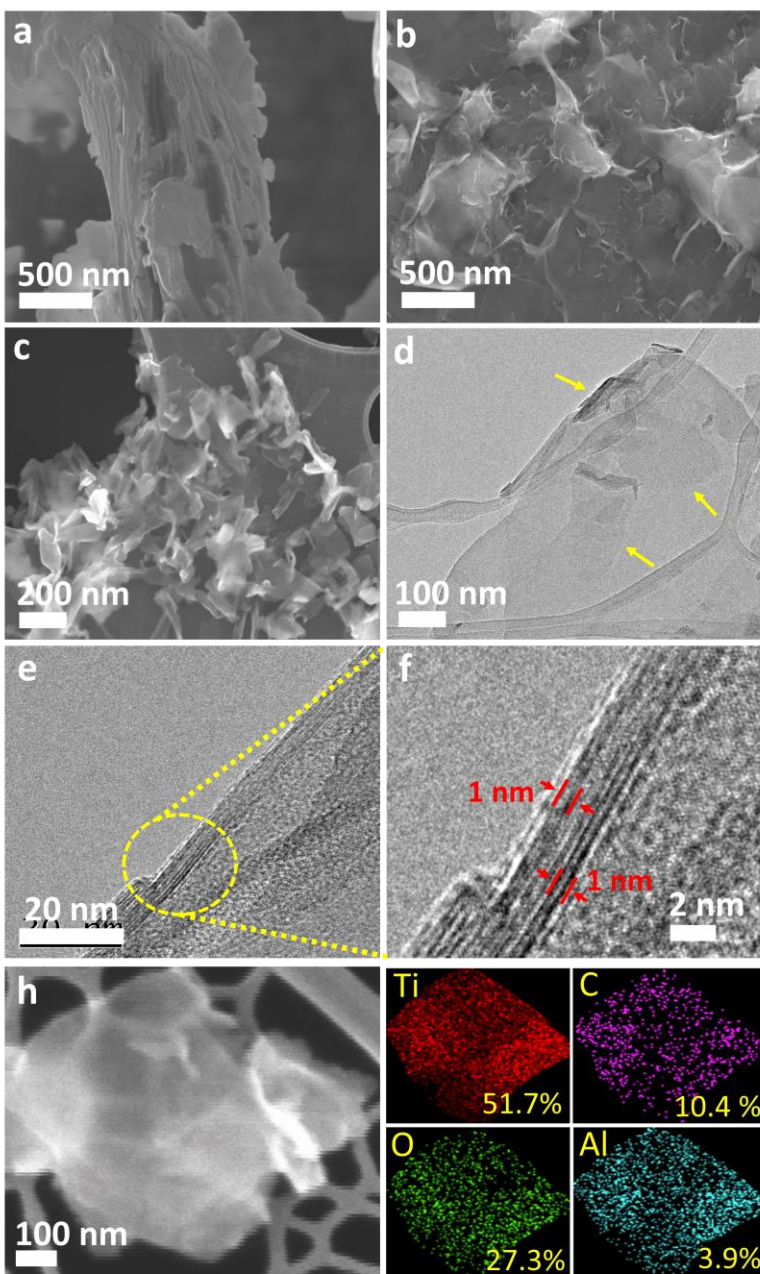


Figure 4.2 SEM images of Ti_3AlC_2 (a) and E- Ti_3AlC_2 (b). (c and d) SEM and TEM images of $\text{Ti}_3\text{C}_2\text{-OH}$ after separating the delaminated sheets via sonication and centrifugation. (e) High-magnification TEM image of a two-layer thick $\text{Ti}_3\text{C}_2\text{-OH}$ and (f) zoom-in TEM image of sheets presented in (e). (h) An SEM image of delaminated $\text{Ti}_3\text{C}_2\text{-OH}$ and the corresponding EDS elemental mapping analysis. Reproduced from reference [46]. Copyright Elsevier 2022.

The XPS survey scan of E-Ti₃AlC₂ reveals the presence of C, Ti, and O (Figure 4.3c); unlike Ti₃AlC₂, no peak corresponding to Al is detected with noticeable increase in O signal. The high-resolution XPS scan in Al 2p region of E-Ti₃AlC₂ (Figure 4.3d) reveals considerable reduction in the intensity of peaks corresponding to Al-Ti (71.5 eV) and Al-O (74 eV) [23]. The peak corresponding to C-Ti in C 1s region of E-Ti₃AlC₂ (Figure 4.3e) shifted to a slightly higher binding energy when compared to that of Ti₃AlC₂, which is consistent with a previous study [34] and attributed to the attachment of functional groups to the Ti₃C₂ surface. In addition, the peak at 454.1 eV in Ti 2p region (Figure 4.3f) corresponding to Ti-Al bond dramatically decreased in intensity for E-Ti₃AlC₂ while the intensity of peaks corresponding to Ti-O at 458.5 eV (Ti 2p_{3/2}) and 464.4 eV (Ti 2p_{1/2}) increased [20, 23]. Peak fitting of high-resolution scan in Ti 2p region of E-Ti₃AlC₂ required multiple components; peak components at 454.4 and 456 eV are attributed to Ti-C and C-Ti-OH bonds, respectively (Figure C4.6d) [35, 36]. This indicates Al removal and formation of Ti₃C₂-OH and TiO₂ after the one-step process. Peak fitting of high-resolution scan in O 1s region of E-Ti₃AlC₂ also confirms the generation of Ti₃C₂-OH after the one-step process (Figure C4.6b). Furthermore, XPS quantitative elemental analysis data (Table C4.1) show that E-Ti₃AlC₂ has lower atomic percentage of Al and higher atomic percentage of O than Ti₃AlC₂, as a result of Al extraction, functional group attachment, and formation of TiO₂. XRD, Raman, and XPS data confirm the successful removal of Al atoms and subsequent generation of Ti₃C₂-OH during the simultaneous etching and delamination process. It is important to mention that the formation of TiO₂ is only detected by XPS as peaks associated with TiO₂ are absent in the Raman spectrum, indicating that the etched portion of the sample consists mainly of T₃C₂-OH and the formation of TiO₂ is limited to the surface. The mild oxidation of MXene may have occurred

during the etching process or post-etching steps (washing, storage, characterization, etc.) as observed in other MXene synthesis studies involving hydrothermal alkali-assisted etching [26, 37].

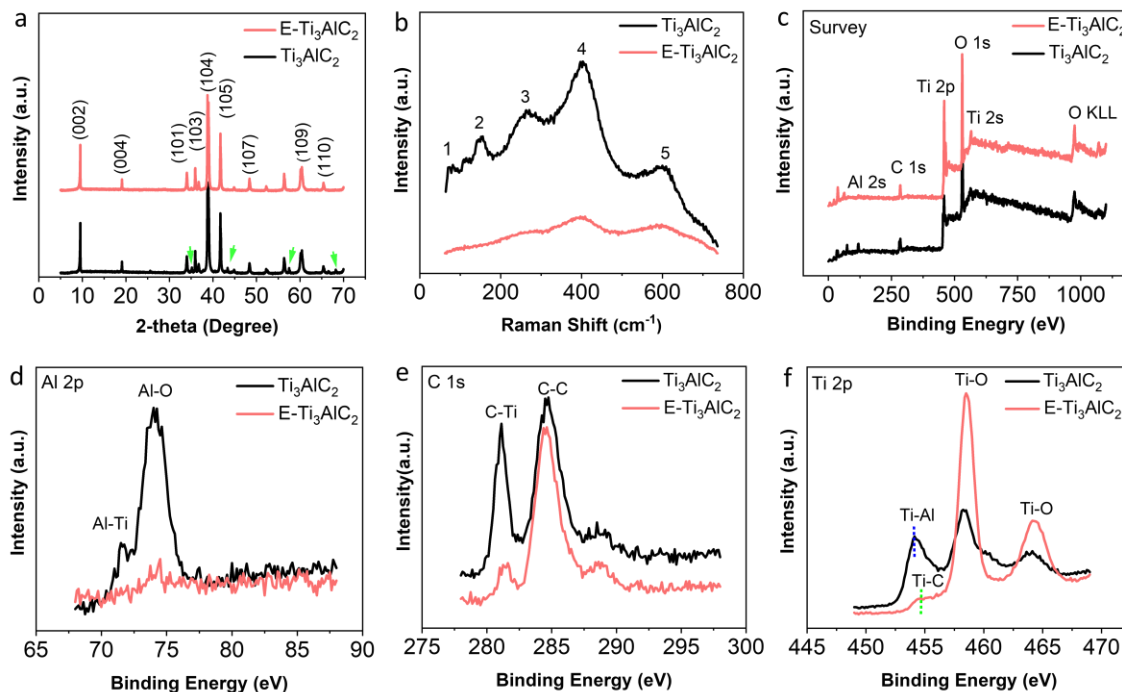
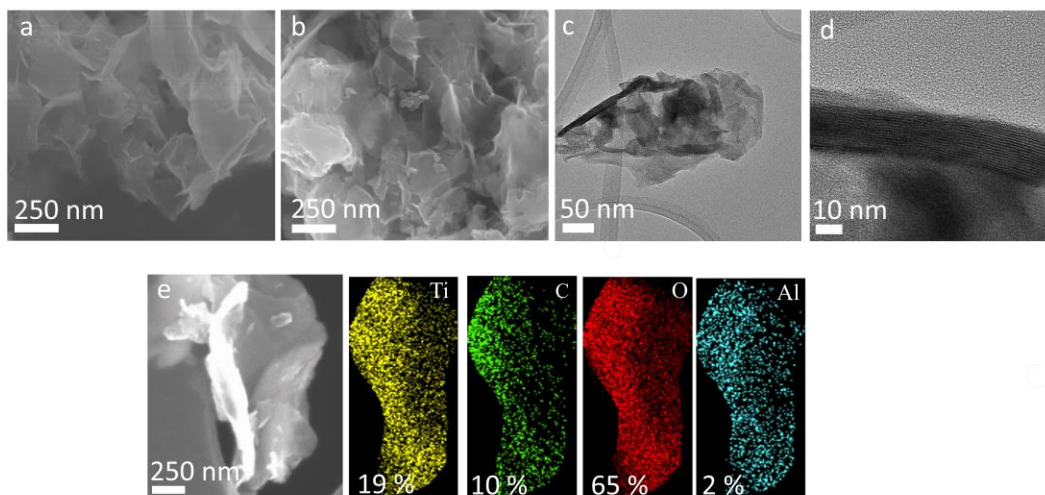


Figure 4.3 Structural and chemical characterization of Ti_3AlC_2 and $\text{E-Ti}_3\text{AlC}_2$. (a) XRD patterns; (b) Raman spectra; (c) XPS survey scans; and high-resolution scans in Al 2p region (d), C 1s region (e), and Ti 2p region (f). Reproduced from reference [46]. Copyright Elsevier 2022.

To compare the efficiency of the one-step process to the two-step, we treated Ti_3AlC_2 with NaOH at 180 °C and then used hydrazine as a delaminating agent in a second step at room temperature. The resulting sample is denoted as $\text{E-Ti}_3\text{AlC}_2\text{-2}$, from which the delaminated $\text{Ti}_3\text{C}_2\text{-OH}$ was collected by sonication and centrifugation steps similar to those used for one-step synthesis of $\text{Ti}_3\text{C}_2\text{-OH}$ (Figure 4.1). Based on initial evidence from the SEM images (Figures 4.4a and 4.4b), superior delamination was achieved with the one-step process. In addition, unlike TEM images in Figure 4.2 that show the generation of thin sheets of $\text{Ti}_3\text{C}_2\text{-OH}$ from the one-step process, TEM images (Figure 4.4c and 4.4d) of $\text{Ti}_3\text{C}_2\text{-OH}$ from the two-step process clearly reveal the

generation of thick sheets. It is noted that XPS analysis of E-Ti₃AlC₂-2 also confirmed Al removal by the two-step process (Figures C4.7).



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Figure 4.4 (a) SEM image of E-Ti₃AlC₂ (one-step), (b) SEM image of Ti₃AlC₂-2 (two-step), (c) TEM image of Ti₃C₂-OH (two-step), (d) high-resolution TEM image of Ti₃C₂-OH (two-step), and (e) a SEM image of Ti₃AC₂-OH (two-step) and the corresponding EDS elemental mapping analysis. Reproduced from reference [46]. Copyright Elsevier 2022.

The low-quality of sheets from delamination using the two-step process is attributed to the interlayer interaction between MXene sheets and subsequent formation of chemical bonds between them. It has been suggested that after Al removal, MXene sheets are stabilized by the formation of bonds with high bonding energy, specifically Ti-Ti and residual Ti-Al bonds, in addition to hydrogen or van der Waals bonds [38]. In the traditional post-etching process, typically conducted at room temperature, the delaminating agent cannot easily surmount the high energy barrier and intercalate between MXene layers. This means that in the absence of an additional driving force such as elevated temperature, the rate of intercalation is relatively slow. In contrast, an instantaneous exchange can occur between Al atoms and the delaminating agent during Al etching in the one-step process in the presence of hydrazine at elevated temperature. The interactions between the sheets and subsequent formation of Ti-Ti and Ti-Al bonds are hindered, resulting in

the formation of delaminated MXene sheets in one step. Our results indicate the one-step process leads to better delamination in comparison to the two-step process, without compromising the efficiency of Al removal. It is meaningful to point out that the addition of an antioxidant to MXene solution is an effective route to mitigate its oxidation during hydrothermal treatment [38]. Because hydrazine is an antioxidant, its presence in the reaction medium is expected to diminish the oxidation of MXene, especially at elevated temperature (i.e. 270 °C) where severe MXene oxidation occurs [23].

Delaminated, $\text{Ti}_3\text{C}_2\text{-OH}$ was obtained from E- Ti_3AlC_2 via sonication and centrifugation as described earlier and coupled with commercial TiO_2 via a facile hydration and dehydration approach to produce a hybrid photocatalyst ($\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$). Based on the XRD data, no peaks corresponding to $\text{Ti}_3\text{C}_2\text{-OH}$ were detected in $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ due to its low content in the hybrid structure (Figure C4.8), consistent with other studies [39, 40]. The diffraction peaks were indexed to several crystal planes of anatase TiO_2 (JCPDS No. 21-1272) and facets of rutile TiO_2 (JCPDS No. 21-1276) [40]. The TEM image of $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ (Figure C4.9a) indicates the TiO_2 particles are supported on $\text{Ti}_3\text{C}_2\text{-OH}$. The high-resolution TEM image (Figure C4.9b) shows the intimate interfacial contact between TiO_2 and $\text{Ti}_3\text{C}_2\text{-OH}$, which is crucial for improved charge carrier mobility in $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ [41]. As expected, no peak corresponding to Al in $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ was detected by XPS as shown in the survey scan (Figure C4.10) [42]. The high-resolution XPS spectra in Ti 2p regions of TiO_2 and $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ demonstrate the Ti 2p doublets of Ti^{4+} ions (Figure C4.11a). The O 1s XPS spectra (Figure C4.11b) reveal the presence of lattice oxygen (529.3 eV) and -OH surface group (531.2 eV). Since Ti and O coexist in TiO_2 and $\text{Ti}_3\text{C}_2\text{-OH}$, the characteristic peaks of Ti and O in $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ are expected to overlap. Because the amount of $\text{Ti}_3\text{C}_2\text{-OH}$ is significantly lower than that of TiO_2 in $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$, the dominant peaks

associated with Ti and O in the XPS analysis of $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ are mainly attributed to TiO_2 . Note that a small amount of C is typically detected in TiO_2 due to the presence of oxygen-containing carbonaceous contaminants (Figure C4.10) [42]. Therefore, C bonds have not been analyzed because it is unclear whether the detected C is from the TiO_2 or $\text{Ti}_3\text{C}_2\text{-OH}$.

Interestingly, the binding energies of Ti 2p and O 1s in $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ showed noticeable shift to lower values compared to those of TiO_2 . The shift is attributed to electron transfer from $\text{Ti}_3\text{C}_2\text{-OH}$ with a low work function to TiO_2 with a high work function, further confirming the intimate interaction between the two components and formation of a metal-semiconductor heterojunction [43, 44]. Xu et al.[44] observed similar shifts in the binding energies of Ti and O when a heterojunction between TiO_2 (high work function component) and CsPbBr_3 (low work function component) was formed via self-assembly coupling. The heterojunction formed in $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ is expected to improve electron-hole separation by allowing the transfer of holes from TiO_2 to $\text{Ti}_3\text{C}_2\text{-OH}$, resulting in improved NO_x photocatalytic oxidation.

The photocatalytic activity of $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ was evaluated and compared to pristine TiO_2 and a hybrid photocatalyst ($\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-F}$) fabricated by coupling TiO_2 with delaminated, F-terminated Ti_3C_2 (most widely used MXene). Detailed characterization of the morphology, composition, and structure of $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-F}$ is summarized in Figures C4.12, C4.13 and C4.14. NO conversion and NO_x storage selectivity for the three photocatalysts at 50% relative humidity under UV light exposure are presented in Figure 4.5a. The performance of the three photocatalysts in the oxidation of NO_x (1 ppm) is expressed in terms of DeNO_x index as shown in Figure 4.5b. Utilizing the DeNO_x index in tandem with relative NO_x oxidation provides a better understanding of the photocatalytic performance. TiO_2 exhibits reasonable NO conversion (53%), but produces massive amount of NO_2 with NO_x storage selectivity of 58% and DeNO_x index of -0.10. Since NO_2

is considerably more toxic than NO, TiO_2 is clearly ineffective as a photocatalyst for NO_x removal. $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-F}$ shows NO_x storage selectivity of 62% and a DeNO_x index of -0.05 at NO conversion of 47%, also indicating its ineffectiveness in photocatalytic NO_x abatement. In contrast, $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ exhibits outstanding performance in NO_x abatement, with excellent NO_x storage selectivity (91%) and a positive DeNO_x index of +0.30 without compromising NO conversion (54%). When compared to other titania-based photocatalysts, tested in the same reactor and under the same conditions, $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ shows superior performance (Figure 4.5c).

A direct comparison of the activity of $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ with other state-of-the-art photocatalysts in the literature can be misleading due to the different reaction conditions used. Therefore, in comparing the NO_x abatement efficiency of the photocatalysts (summarized in Table C4.2), the initial concentration of NO, catalyst loading, relative humidity, and emission spectrum of the light source have been considered. Reaction time is also an important factor because it affects conversion. The longer the reaction time, the lower the conversion due to photocatalyst deactivation caused by the accumulation of reaction products on the catalyst surface. Hence, for proper evaluation of the catalyst performance, we have allowed the photocatalytic reaction to run for a long period (120 minutes) and the averages of the data obtained are used to calculate NO conversion, selectivity, and DeNO_x index. The data presented in Table C4.2 show that our photocatalyst ($\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$) exhibits outstanding activity in terms of selectivity and DeNO_x with comparable NO conversion over the longest reaction time.

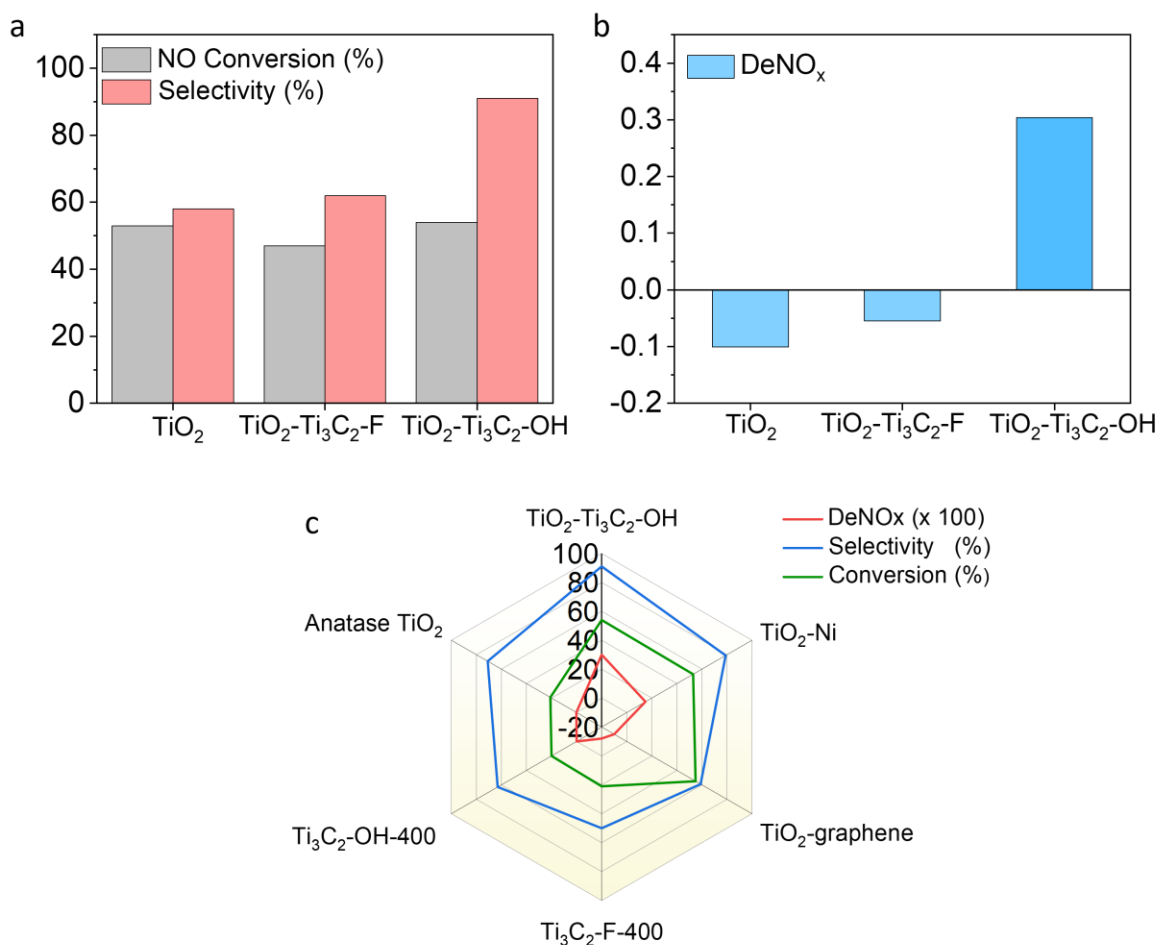
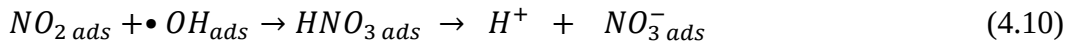
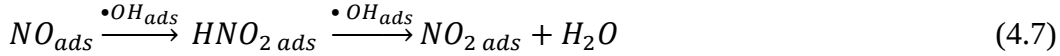
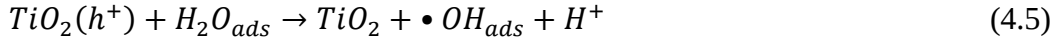


Figure 4.5 (a) NO conversion and NO_x storage selectivity and (b) DeNO_x index for TiO₂, TiO₂-Ti₃C₂-F, and TiO₂-Ti₃C₂-OH. (c) Spider chart comparing the performance of TiO₂-Ti₃C₂-OH with other titania-based photocatalysts. Reproduced from reference [46]. Copyright Elsevier 2022.

To rationalize the stark difference in photocatalytic performance of TiO₂, TiO₂-Ti₃C₂-F, and TiO₂-Ti₃C₂-OH and gain insight into the superior performance of TiO₂-Ti₃C₂-OH, it is necessary to consider the mechanism of NO_x oxidation [18, 45, 46]. The first of three steps in the photocatalytic oxidation of NO_x is the generation of charge carriers on TiO₂ surface upon light exposure (Equation 4.4). The second step is the formation of ROS via the reaction between the photogenerated charge carriers and water/oxygen molecules adsorbed on TiO₂ surface (Equations

4.5-4.6). The third step is the oxidation of NO adsorbed on TiO₂ surface to NO₂ and $NO_3^-_{ads}$ (Equations 4.7-4.10).



In addition to the generation of charge carriers upon light exposure and subsequent oxidation of NO_x by ROS, it is clear from the mechanism that the adsorption of H₂O on Photocatalyst surface is a significant step. The conversion rate of NO does not depend on H₂O adsorption, however, the conversion of NO₂ does. In fact, it has been shown that H₂O can displace NO₂ from TiO₂ surface [45], a phenomenon that can prevent the interaction between the NO₂ produced and ROS, and consequently, inhibit NO_x storage selectivity. In addition, the potential dissociation of adsorbed water molecules on oxygen vacancies of TiO₂ may lead to the formation of bridging OH terminals that trap electrons and facilitate their recombination with holes, and hence, reduce the concentration of ROS available for NO_x oxidation [18]. Note that reduction in ROS concentration can also occur via direct electron-hole recombination without the contribution of H₂O in TiO₂ [47]. The low amount of ROS initiates the oxidation of NO to NO₂ (Equations 4.7 and 4.8), but is insufficient to store the NO₂ in the form of $NO_3^-_{ads}$ on the surface of TiO₂ (Equations 4.9 and 4.10) resulting in release of NO₂ into the atmosphere. Therefore, the low

DeNO_x index of TiO₂ can be correlated to (1) desorption of NO₂ produced from TiO₂ surface by adsorbed H₂O and (2) H₂O-assisted/non-H₂O-assisted charge carrier recombination.

In the case of TiO₂-Ti₃C₂-OH, NO₂ can also be displaced by H₂O from TiO₂ surface in the same manner as described above for pristine TiO₂; however, the desorbed NO₂ adsorbs on OH terminals of Ti₃C₂ where it accepts an electron and is non-photocatalytically stored in the form of $NO_2^-_{ads}$ [8]. The same OH terminals may also act as sacrificial sites for H₂O adsorption, alleviating the competitive adsorption between NO₂ and H₂O on TiO₂, which in turn mitigates the displacement of NO₂ from TiO₂ and facilitates its subsequent oxidation. Furthermore, Ti₃C₂-OH is a known hole scavenger due to its ultralow work function [11, 12, 48]. Therefore, Ti₃C₂-OH in TiO₂-Ti₃C₂-OH can accept the holes and prohibits their consumption via recombination with electrons, evidenced by the observed quenching in the photoluminescence (PL) intensity and increase in the transient photocurrent density of TiO₂ after coupling with Ti₃C₂-OH (Figure C4.15a and b). Consequently, TiO₂-Ti₃C₂-OH is expected to have a higher amount of charge carriers on the surface to support the generation of more ROS for NO_x photooxidation and subsequent formation of $NO_3^-_{ads}$. Formation of $NO_3^-_{ads}$ can also occur via the oxidation of $NO_2^-_{ads}$ that is non-photocatalytically adsorbed on Ti₃C₂-OH. In contrast to TiO₂, high-resolution XPS scan in N 1s region of TiO₂-Ti₃C₂-OH obtained after the photocatalytic reaction (Figure 4.6a) shows the presence of $NO_3^-_{ads}$ on the surface, confirming the solid-state storage of NO_x on TiO₂-Ti₃C₂-OH. The presence of $NO_3^-_{ads}$ on the surface of the used TiO₂-Ti₃C₂-OH is also confirmed by FT-IR spectroscopy (Figure 4.6b). After the photocatalytic reaction, the binding energies of Ti 2p and O 1s spectra for TiO₂-Ti₃C₂-OH show a slight shift to higher values compared to those of fresh TiO₂-Ti₃C₂-OH (Figure C4.11a and b). After the reaction, however, the binding energies of Ti 2p and O 1s for TiO₂-Ti₃C₂-OH are still lower than those of the fresh TiO₂. This observation suggests the

accumulation of electrons on TiO_2 in the used $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ and that the photocatalytic process did not impact the ability of $\text{Ti}_3\text{C}_2\text{-OH}$ to act as a hole reservoir.

Excellent NO_x abatement is therefore achieved with $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ due to its ability to facilitate oxidation of NO_x via photocatalytic and non-photocatalytic routes as schematically depicted in Figure 4.6c. For $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-F}$, even though $\text{Ti}_3\text{C}_2\text{-F}$ can reduce electron-hole recombination as shown by Ye et al.[39] and confirmed by our PL data (Figure C4.16), other studies [7, 8] have also shown that the presence of F terminals on the surface is unfavorable for NO_2 adsorption. Hence, it is reasonable to assume that less NO_2 molecules were adsorbed on $\text{Ti}_3\text{C}_2\text{-F}$ in comparison to $\text{Ti}_3\text{C}_2\text{-OH}$, and consequently, reduced the ability of $\text{Ti}_3\text{C}_2\text{-F}$ to store the produced NO_2 by the photocatalytic and non-photocatalytic routes, resulting in poor NO_x abatement. It is highlighted that the aged $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ exhibits lower NO_2 conversion and less stable performance compared to that of the fresh $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$. This observation may be attributed to the partial oxidation of $\text{Ti}_3\text{C}_2\text{-OH}$ that gradually occurs in air, which results in the deterioration in NO_x removal performance via photocatalytic and non-photocatalytic pathways. Nevertheless, the aged $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ shows a higher performance than the fresh TiO_2 and fresh $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-F}$ (Figure 4.7).

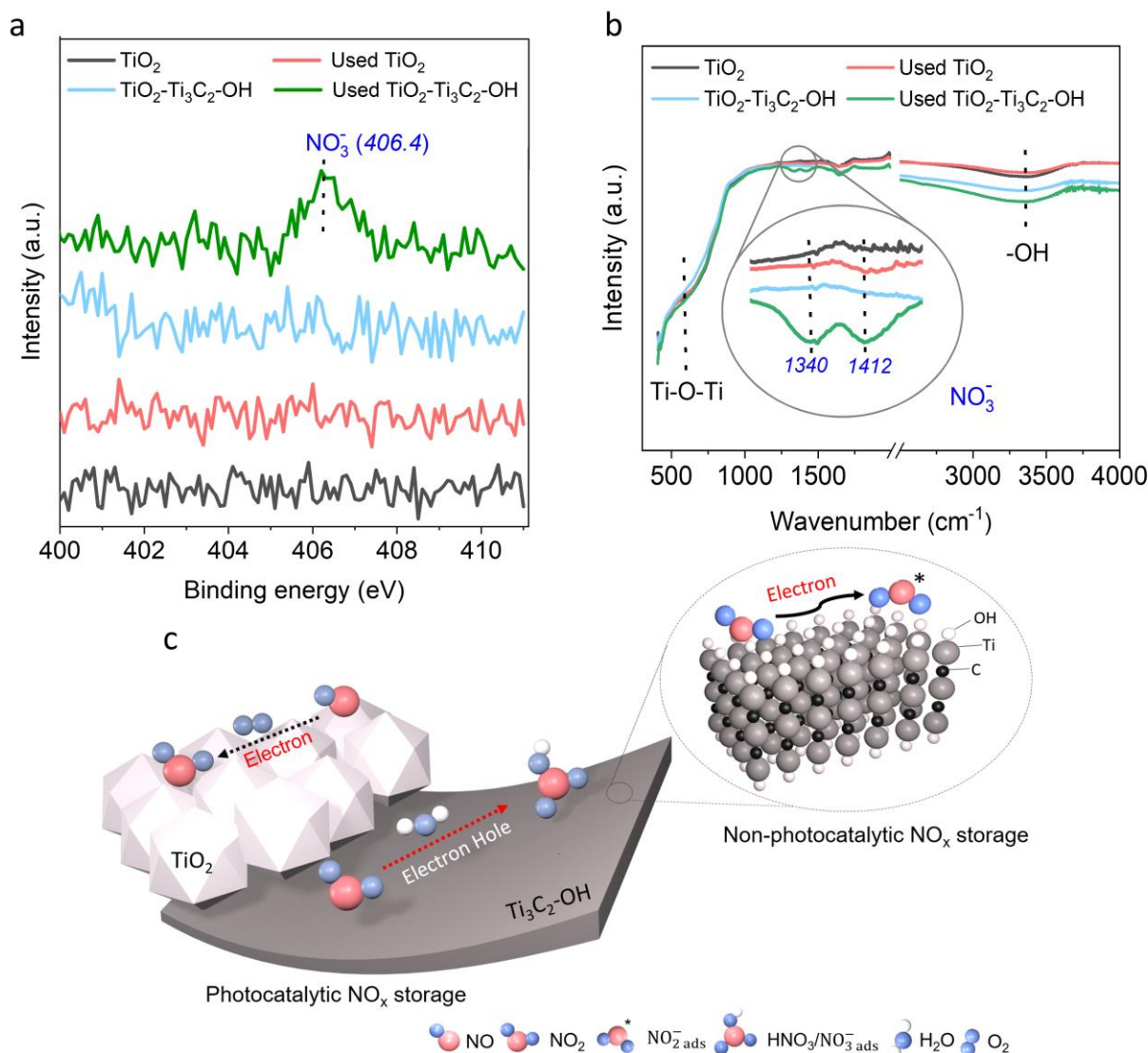


Figure 4.6 (a) High-resolution XPS scan in N 1s region of TiO₂ and TiO₂-Ti₃C₂-OH before and after the photocatalytic reaction, (b) FT-IR spectra of TiO₂ and TiO₂-Ti₃C₂-OH before and after the photocatalytic reaction, and (c) schematic illustration of NO_x abatement by TiO₂-Ti₃C₂-OH; for the sake of simplicity, the oxidation of NO to HNO₃ by photogenerated electrons and the oxidation of NO to NO₂ by photogenerated holes are not shown in the schematic. Reproduced from reference [46]. Copyright Elsevier 2022.

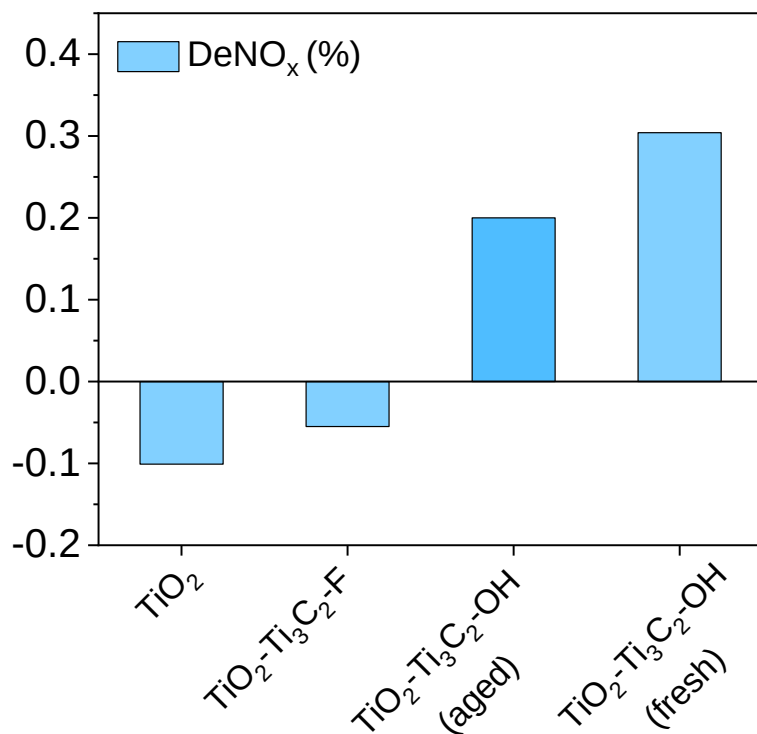


Figure 4.7 DeNO_x index for TiO₂, TiO₂-Ti₃C₂-F, TiO₂-Ti₃C₂-OH (aged), and TiO₂-Ti₃C₂-OH. Reproduced from reference [46]. Copyright Elsevier 2022.

4.4 Conclusions

In summary, we have developed a facile, fluorine-free, and efficient approach to fabricate Ti₃C₂-OH. The fabrication methodology involves simultaneous etching of Al from MAX phase and intercalation with hydrazine and/or its derivative to produce thin-layered MXene. Coupling Ti₃C₂-OH with TiO₂ yields a hybrid structure (TiO₂-Ti₃C₂-OH) that exhibits outstanding NO_x abatement, evidenced by NO_x storage selectivity and DeNO_x index that are superior to several other state-of-the-art titania-based photocatalysts, including hybrid photocatalysts synthesized with traditional MXene. The single-step process demonstrated in this study will not only enhance fabrication of high-quality Ti₃C₂-OH, but also reduce time and effort associated with traditional techniques that comprise two steps especially if F-group reduction is required. In addition, this

work demonstrates the pivotal role $\text{Ti}_3\text{C}_2\text{-OH}$ plays as a co-catalyst with TiO_2 and paves a way for potential use of $\text{TiO}_2\text{-MXene}$ hybrids in practical photocatalytic NO_x removal.

4.5 References

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Chapter 5 - TiO₂-g-C₃N₄ Photocatalysts with Purification Effect for NO_x Oxidation

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5.1 Introduction

Air pollution is a considerable environmental health threat in the United States, linked with the deaths of 100000–200000 individuals per year [1]. Nitrogen oxides (NO_x) are among the most serious air pollutants that impact human respiratory systems and serve as precursors for ozone and haze formation [2, 3]. A significant portion of NO_x is generated anthropogenically by high-temperature processes involving the presence of nitrogen and oxygen, such as industrial furnaces, combustion engines, and oil- or gas-fired heating [4, 5]. Various approaches for NO_x removal have been suggested, such as plasma-assisted catalysis, solid-liquid adsorption, and catalytic/non-catalytic reduction [6-8]. However, these processes treat NO_x only at the emission source where the concentrations of NO_x are in hundreds of ppb and necessitate the use of high temperatures or complex tools for abatement. Photocatalytic oxidation is an effective alternative for NO_x removal at sub-ppb levels under ambient atmospheric conditions. Coating a photocatalyst on concretes and buildings is expected to effectively remove NO_x from the air at a low cost through the utilization of renewable solar energy. In addition, combining photocatalysis with one of the conventional approaches mentioned above is expected to provide a new pathway for effective removal of large amounts of NO_x from industrial flue gas. However, the limited visible light absorption and low

NO_x adsorption capacity of currently available photocatalysts hamper their utilization in practical NO_x oxidation.

The unique characteristics of graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) including its non-toxicity, high chemical and thermal stability, facile synthesis, remarkable light absorption (band gap of 2.7 eV), and low cost [9, 10], rendering it a potential visible light active photocatalyst. However, the photo-reactivity of $\text{g-C}_3\text{N}_4$ is hampered by the high recombination rate of photo-induced electron-hole pairs [11, 12]. Utilizing TiO_2 as a cocatalyst with $\text{g-C}_3\text{N}_4$ is an effective route to mitigate charge carrier recombination and boost the overall photocatalytic activity. Charge transfer between $\text{g-C}_3\text{N}_4$ and TiO_2 depends on the type of heterojunction between them. In Z-scheme heterojunction, photoexcited electrons in the conduction band (CB) of TiO_2 migrate to recombine with the photoexcited holes in the valence band (VB) of $\text{g-C}_3\text{N}_4$ at the interface of TiO_2 - $\text{g-C}_3\text{N}_4$. TiO_2 - $\text{g-C}_3\text{N}_4$ photocatalyst with a Z-scheme heterojunction has attracted attention because of the good visible light absorption, promoted reaction kinetics, strong reduction and oxidation ability, and improved charge carrier dynamics [13-15]. Z-scheme TiO_2 - $\text{g-C}_3\text{N}_4$ hybrids have therefore been utilized in a variety of visible light-assisted photocatalytic processes such as CO_2 conversion, bacterial inactivation, water treatment, and air purification [16-19].

NO_x photocatalytic oxidation is a multistep reaction involving the conversion of NO (g) to NO_2 (g) followed by the conversion of NO_2 to NO_3^- (s). NO_3^- is the solid-state form of NO_x , which accumulate (store) on the photocatalyst surface during the reaction, reducing the number of available adsorption sites for NO or NO_2 oxidation and compromising the overall activity of NO_x oxidation. The photocatalyst should have a high NO_x adsorption capacity for effective NO_x oxidation. Unfortunately, TiO_2 and $\text{g-C}_3\text{N}_4$ have low NO_x adsorption capacity [20, 21], indicating the limitation of TiO_2 - $\text{g-C}_3\text{N}_4$ hybrid with conventional morphology as a photocatalyst for NO_x

oxidation. In fact, the Z-scheme hybrid photocatalyst formed by coupling TiO_2 and $\text{g-C}_3\text{N}_4$ showed limited activity in NO_x oxidation under visible light. To overcome this challenge, Papailias et al.[22] proposed the coupling of TiO_2 - $\text{g-C}_3\text{N}_4$ with a NO_x storage domain such as CaCO_3 . Although this domain improves NO_x storage capacity, its presence reduces the amount of the photo-active components (TiO_2 and $\text{g-C}_3\text{N}_4$) in the photocatalyst and may subsequently reduce the number of charge carriers. In addition, the NO_x storage domain can intervene between TiO_2 and $\text{g-C}_3\text{N}_4$, reducing the quality of the formed Z-scheme junctions and undermining charge carrier transfer. Recently, Hu et al.[23] suggested the utilization of ultra-low work function 2D MXene (titanium carbide MXene) as a hole reservoir and NO_x storage domain with TiO_2 - $\text{g-C}_3\text{N}_4$. In this ternary structure, the MXene is adapted to facilitate charge carrier separation by accepting the holes from TiO_2 - $\text{g-C}_3\text{N}_4$, and at the same time, serve as a storage domain for the formed NO_3^- . However, the MXene is characterized by its low stability and tends to speedily oxidize under ambient condition to form TiO_2 and carbonaceous compounds, creating obstacles in front of its utilization in practical NO_x oxidation [24]. Further, the transfer of holes from TiO_2 to MXene reduces their oxidation power and thereby, their ability to oxidize NO_x species. Therefore, an alternative approach is required to design TiO_2 - $\text{g-C}_3\text{N}_4$ with high NO_x adsorption capacity while maintaining its intrinsic properties.

NO_x oxidation is not only controlled by NO_x adsorption capacity but also by H_2O adsorption on the photocatalyst surface. H_2O plays a key role in NO_x oxidation as it traps the photoexcited holes to form active radicals ($\bullet\text{OH}$), which is essential for NO_x oxidation. Therefore, a high concentration of H_2O is expected to boost NO_x oxidation. However, H_2O possesses higher polarity than NO or NO_2 , and consequently, it can displace them from photocatalyst surface during the reaction impeding their oxidation. As a result, there is a huge inconsistency in the literature

regarding the role of H₂O in NO_x oxidation [25-28]. Although recent studies examined NO_x oxidation by Z-scheme TiO₂-g-C₃N₄ as mentioned earlier, the correlation between H₂O concentration and photocatalytic NO_x oxidation remains unclear and yet to be explored.

Recently, hierarchical porous materials have appeared as an appealing family of functional structures in gas sensing, separation, catalysis/photocatalysis, biomedicine, adsorption, and energy storage [15, 29-31]. Due to their accessible structure, multiscale porosity, and large surface area, these hierarchical materials are efficient in adsorbing and hosting reaction species. Hence, we hypothesize that coupling hierarchical porous TiO₂ with g-C₃N₄ will lead to the formation of a hybrid photocatalyst with high NO_x adsorption capacity while reducing charge carrier recombination in g-C₃N₄, and hence, exhibit effective NO_x oxidation under visible light. Herein, a hierarchical macro-mesoporous structure composed of Z-scheme TiO₂-g-C₃N₄ hybrid embedded in parallel TiO₂ channels was synthesized and used for the first time in NO_x photocatalytic oxidation in a continuous flow reactor. The unique structure of the photocatalyst provides efficient channels for NO_x adsorption and storage of NO_x oxidation products (i.e., NO₃⁻(s)). The photocatalytic reaction was carried out under concurrent exposure to blue and green lights (cyan light) and 50% relative humidity (RH) which is representative of outdoor humidity levels in most urban cities, as shown in our previous study [27]. The “DeNO_x index” is used to evaluate the overall NO_x oxidation activity by considering both NO conversion and NO₂ formation. To develop a mechanistic understanding of photocatalytic NO_x oxidation that will benefit the practical application of the technology, we also investigated the impact of RH on photocatalytic NO_x reaction.

5.2 Experimental Section

5.2.1 Photocatalyst Synthesis

The TiO_2 -g- C_3N_4 heterojunction photocatalyst was synthesized following a procedure reported elsewhere [15]. In brief, the first step involved using a sol-gel process to form the porous TiO_2 framework. About 20 mL of tetrabutyl titanate (Sinopharm Chemical Reagent Co., Ltd., China) was stepwise poured into distilled water (200 mL) and incubated for 36 hours at 25 °C. TiO_2 precipitate was filtered, rinsed, and dried in an oven at 60 °C for 12 hours. This resulted in a dry TiO_2 powder with a hierarchical internal structure consisting of aligned macro-channels and mesoporous walls. In the second step, 3.0 g of melamine precursor was dispersed in hot distilled water (100 mL) and mixed with 0.50 g of the hierarchical TiO_2 powder. The solution was dried in an oven at 100 °C for 12 hours, and the resultant powder was calcined at 550 °C for 2 hours under air to yield a yellow-colored TiO_2 -g- C_3N_4 photocatalyst. g- C_3N_4 and TiO_2 porous powders were prepared by calcining the melamine precursor and the dried white TiO_2 precipitate after step 1, respectively, at 550 °C for 2 hours.

5.2.2 Characterization

The morphology of the samples was characterized using Topcon/ISI/ABT DS 130F field emission scanning electron microscope (FESEM) (Akashi Beam Technology Corporation, Tokyo, Japan) and Tecnai Osiris (Scanning) Transmission Electron Microscope operating at 200 kV (FEI, Hillsboro, OR, USA). The crystal structure of the photocatalysts was examined using Bruker AXS D8 Advance Discover Diffractometer (Bruker Corporation, Karlsruhe, Germany) with a $\text{Cu K}\alpha$ radiation of wavelength 0.15418 nm and a detector slit width of 1 mm. XRD reference spectra from Joint Committee on Powder Diffraction Standard (JCPDS) were used for analysis. The composition of the samples was determined using a Thermogravimetric Analyzer (TGA) Q50

system (TA Instruments - Waters LLC, New Castle, DC) at room temperature to 900 °C in an air atmosphere. The optical properties of the photocatalysts were characterized using Cary 500 UV-VIS-NIR spectrophotometer with a diffuse reflectance accessory (Agilent Technologies, CA, USA). The surface chemical composition was characterized using a PHI 5000 Versa XPS system (Chanhassen, MN) with a monochromatized Al K α source (1486.7 eV). All the XPS spectra were obtained using a 400 μ m spot size. 200 eV pass energy with 1 eV step was used to collect the survey scans. 50 eV pass energy with 0.1 eV step was utilized to collect the high-resolution spectra. A convolution of Gaussian and Lorentzian peaks was used to represent the fitted peak, while the background was subtracted by Shirley function. The standard sp² C 1s peak at 284.80 eV was used to charge correct the XPS spectra. Raman spectra were acquired with a DXRTM Raman microscope (Thermo Fisher Scientific, Madison, WI) with a 780 nm laser at a power of 1 mW, using a 10 $\times$ objective lens with a slit width of 25 μ m. Multimode microplate reader SpectraMax i3x was used to acquire photoluminescence spectra over the range of 400-700 nm using different excitation wavelengths.

5.2.3 Photocatalyst Performance Evaluation

5.2.3.1 Substrate Preparation

Samples were ground and dispersed in ethanol (30 mg/ml) by ultrasonication. Each dispersion was dropped onto a glass slide (37.5 cm²) and cast to 250 μ m thin film by the doctor blade. The slides coated with the photocatalysts were dried under ambient conditions before subsequent usage.

5.2.3.2 Reactor Configuration

A continuous-flow reactor built following ISO standards made of steel and equipped with a quartz glass window to allow light-photocatalyst interaction was used to perform the NO_x

photocatalytic oxidation reaction. Two gas cylinders were connected to the reactor (100 ppm NO in N₂, and breathing air). The flow rate of gases to the reactor was monitored by mass flow controllers. The humidity on the inlet gas mixture was measured by a sensor-push HT1 humidity sensor. A chemiluminescent 42C Low Source analyzer (Thermo Fisher Scientific) was employed to measure the concentration of NO and NO₂ during reaction time.

5.2.3.3 Activity Measurement

A photocatalyst coated on a glass slide was placed in a sample holder and loaded into the reactor. 1.0 ppm NO was introduced into the reactor at a total airflow of 1000 sccm and 50 % relative humidity, and allowed to equilibrate. The reaction was then commenced by light exposure and continued for 30 minutes. The concentration of NO and NO₂ was calculated by taking the average of all the data obtained during the oxidation reaction.

5.3 Results and Discussion

The morphology of TiO₂ and TiO₂-g-C₃N₄ was studied using FESEM. The TiO₂ possesses a unique architecture of aligned channel-like pores of about 3 μm in diameter and greater than 20 μm in length with walls that are porous (Figure 5.1 a and b). BET analysis revealed that TiO₂ comprises mesopores of 2-8 nm. The aligned open channels and combined macro-mesopores are expected to facilitate faster diffusion of gaseous phase NO_x. As observed in Figure 5.1b, a smaller portion of TiO₂ exists as spherical nanoparticles inside the aligned macropores. In the TiO₂-g-C₃N₄ hybrid, the aligned macropores of TiO₂ were partially filled, and the TiO₂ walls were coated uniformly with g-C₃N₄ (Figures 5.1 c and d). The aligned pores of TiO₂ facilitated the homogeneous coverage of g-C₃N₄ throughout the pore surfaces by allowing the precursors of g-C₃N₄ to infiltrate into the pores easily. The TEM image in Figure 5.1e shows that the spherical TiO₂ nanoparticles are intimately coupled with g-C₃N₄. The intimate interaction between TiO₂ and

g-C₃N₄ is further demonstrated by the HRTEM image (Figure 5.1f), in which TiO₂ nanoparticles are anchored on g-C₃N₄. This type of interaction between TiO₂ and g-C₃N₄ is essential for forming a highly effective Z-scheme heterojunction. Both the porous structure and effective heterojunction of the TiO₂-g-C₃N₄ hybrid make it suitable as an efficient photocatalyst for NO_x oxidation.

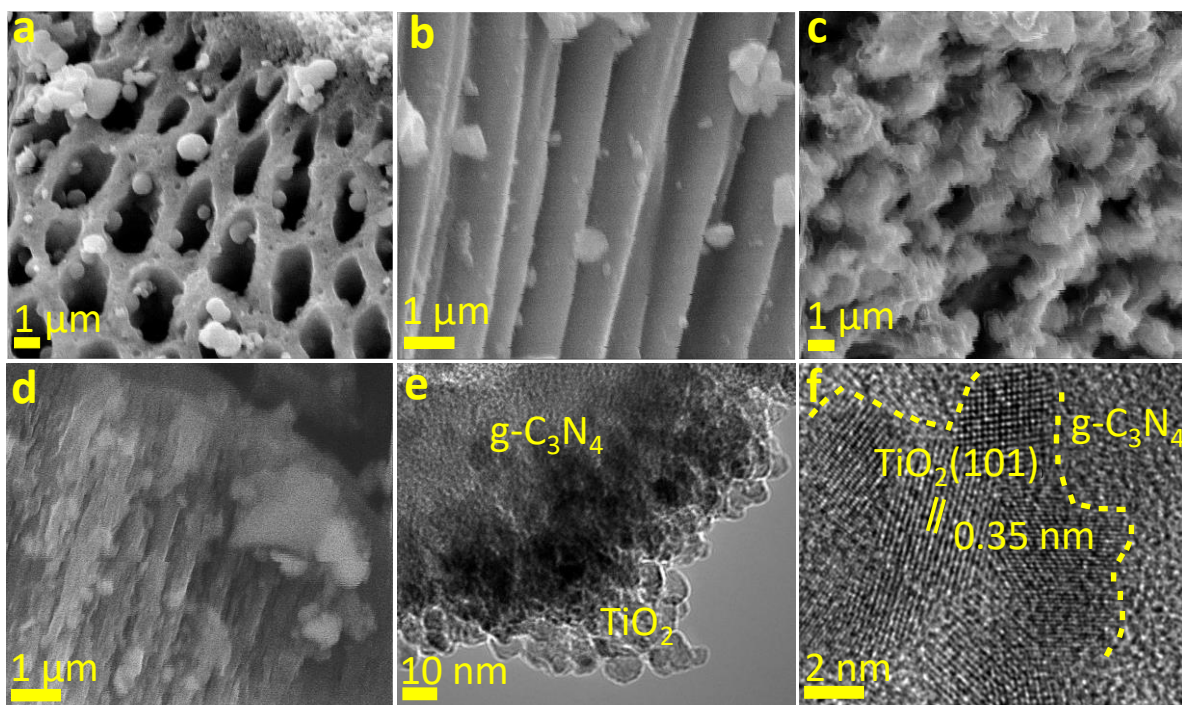


Figure 5.1 Morphological characterization of photocatalysts: (a) an SEM image of TiO₂ surface, (b) a cross-sectional SEM image of TiO₂ shown in (a), (c) an SEM image of TiO₂-g-C₃N₄ surface, (d) a cross-sectional SEM image of TiO₂-g-C₃N₄, shown in (c), (e) a TEM image of the interface between TiO₂ and g-C₃N₄ in TiO₂-g-C₃N₄, and (f) the HR-TEM of the interface in (e).

The isotherms of N₂ adsorption-desorption and distributions of pore size of TiO₂, g-C₃N₄, and TiO₂-g-C₃N₄ are shown in Figures 5.2a and 5.2b. Based on the determination of IUPAC [32], all samples showed Type IV-isotherms, proposing the presence of mesopores. The g-C₃N₄ showed an H3-type hysteresis loop isotherm, signaling the presence of “slit-like” pores [15]. Conversely, TiO₂ showed an isotherm with an H2-type hysteresis loop, which was attributed to the “ink-bottle-

like” pores likely formed between the TiO_2 sphere in the aligned channels of the hierarchical structure [15]. Interestingly, $\text{TiO}_2\text{-g-C}_3\text{N}_4$ demonstrated a unique structure represented by a hysteresis loop with a combination of H2- and H3-type isotherms. The H2-type loop in the pressure range of 0.4–0.8 is attributed to the “ink-bottle-like” structure from the TiO_2 channel occupied with $\text{TiO}_2/\text{g-C}_3\text{N}_4$ aggregates. The H3-type loop in the pressure range of 0.9–1.0 is ascribed to “slit-shaped” pores between the connected structures. $\text{TiO}_2\text{-g-C}_3\text{N}_4$ exhibited a largest pore volume ($0.008 \text{ cm}^3/\text{g}$) and higher surface area ($50.4 \text{ m}^2/\text{g}$) than the pristine $\text{g-C}_3\text{N}_4$, whose largest pore volume and surface area are $0.002 \text{ cm}^3/\text{g}$ and $48.7 \text{ m}^2/\text{g}$, respectively. The increase in pore volume and surface area of $\text{g-C}_3\text{N}_4$ upon coupling with TiO_2 is crucial for storing NO_x species and minimizing NO_2 formation.

Figure 5.2c shows the isothermal adsorption behavior of $\text{g-C}_3\text{N}_4$, TiO_2 , and $\text{TiO}_2\text{-g-C}_3\text{N}_4$. NO is used as a representative of NO_x . All samples showed breakthrough time, indicating the favorable NO adsorption on them. The breakthrough time is defined as the time needed to detect NO within the effluent. Generally, the longer the breakthrough time, the better the storage capacity of a catalyst. The breakthrough time of TiO_2 and $\text{TiO}_2\text{-g-C}_3\text{N}_4$ was longer than that of $\text{g-C}_3\text{N}_4$, indicating their high NO adsorption capacity. Interestingly, $\text{TiO}_2\text{-g-C}_3\text{N}_4$ exhibited almost identical breakthrough time to TiO_2 , suggesting coupling $\text{g-C}_3\text{N}_4$ and TiO_2 as an efficient pathway to form a photocatalyst with high NO adsorption capacity. It is also observed that the NO saturation times of TiO_2 (12 min) and $\text{TiO}_2\text{-g-C}_3\text{N}_4$ (10 min) are longer than that of $\text{g-C}_3\text{N}_4$ (7 min), further validating the ability of TiO_2 and $\text{TiO}_2\text{-g-C}_3\text{N}_4$ to adsorb NO effectively. The NO adsorption capacity of the photocatalyst samples was estimated using Equations 5.1 and 5.2 [33], and the results are shown in Figure 5.2d.

$$qe = \frac{C_o \times M_{NO} \times P \times F \times S \times 10^{-3}}{R \times T \times W} \quad (5.1)$$

$$S = \int_0^t (1 - \frac{C_{NO}}{C_o}) dt \quad (5.2)$$

where q_e is the NO adsorption capacity (mg/g), C_o is the inlet NO concentration (ppm), P is the reaction pressure (Pa), M_{NO} is the NO molar mass (30 g/mol), F is the module flow gas rate (m³/s), T is the reaction temperature (25 °C), R is the ideal gas constant (8.314 J/mol·K), S is the integrated area of the adsorption curve, and W_{cat} is the catalyst load mass (g), C_{NO} is the outlet NO concentration (ppm), and t is the adsorption time (s). The results reveal that the adsorption capacity of TiO₂ (0.0074 mg/g) and TiO₂-g-C₃N₄ (0.0062 mg/g) is higher than that of g-C₃N₄ (0.0043 mg/g). This observation further confirms the improvement in the NO_x adsorption capacity of g-C₃N₄ upon coupling with TiO₂. Therefore, TiO₂-g-C₃N₄ is expected to store NO oxidation products during the photocatalytic reaction effectively.

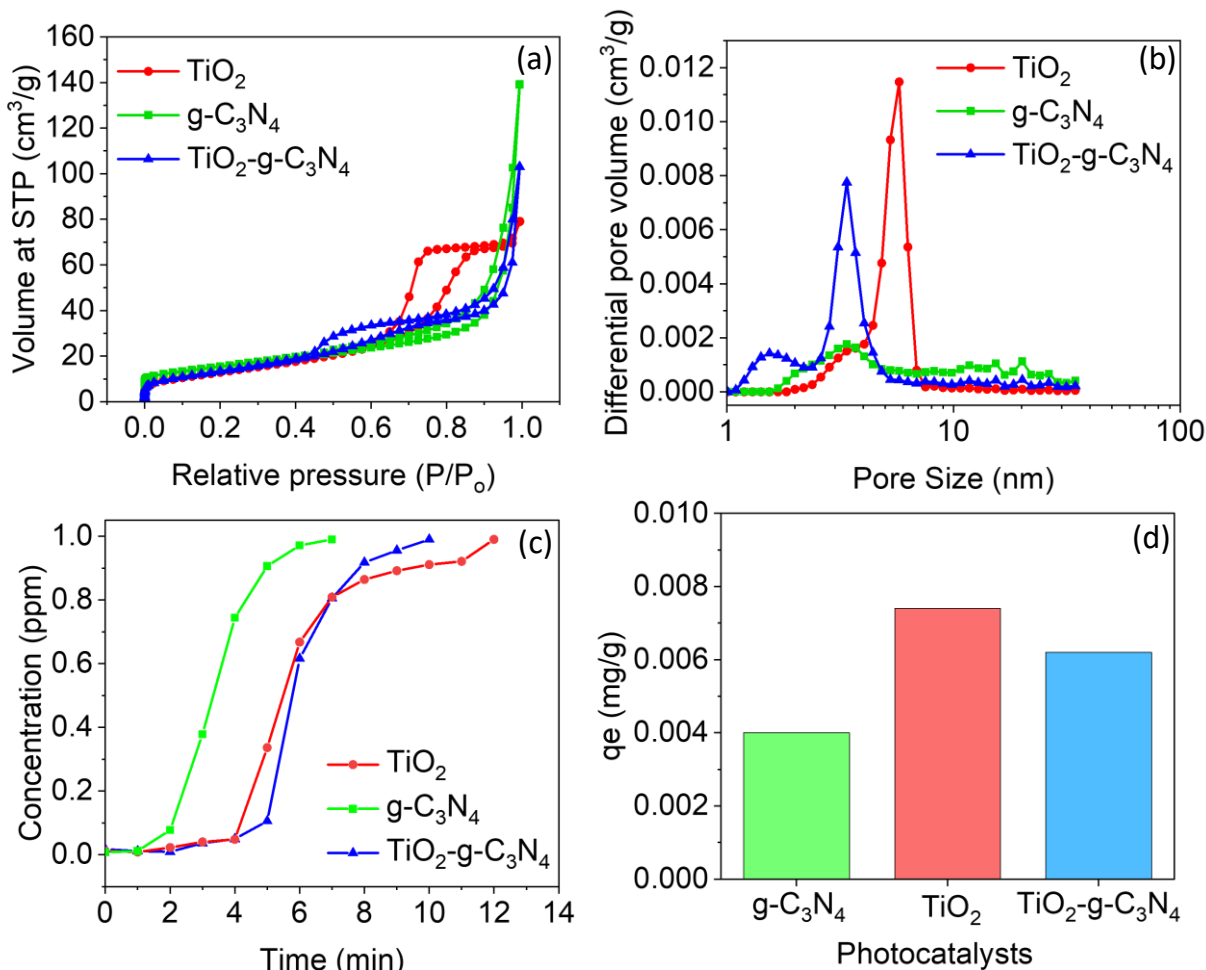


Figure 5.2 (a) N₂ adsorption-desorption isotherms of TiO₂, g-C₃N₄, and TiO₂-g-C₃N₄. (b) Pore size distributions of TiO₂, g-C₃N₄, and TiO₂-g-C₃N₄. (c) Isothermal NO adsorption profiles of TiO₂, g-C₃N₄, and TiO₂-g-C₃N₄ and (d) a histogram of their NO adsorption capacity.

XRD is used to probe the crystal structure of the samples, as depicted in Figure 5.3 a. The TiO₂ sample showed the characteristic diffraction peaks at 25.3°, 36.9°, 37.8°, 38.6°, 48.0°, 53.9°, 55.1°, 62.1°, 62.7°, and 68.7° that correspond to (101), (103), (004), (112), (200), (105), (211), (213), (204), and (116) planes of TiO₂ anatase (JCPDS# 21-1272). The g-C₃N₄ sample showed two characteristic diffraction peaks at 13.1° and 27.6° corresponding to the (100) and (002) planes of g-C₃N₄, respectively. The TiO₂-g-C₃N₄ hybrid sample has diffraction peaks at 25.3°, 13.1°, and 27.6° that are characteristic of both g-C₃N₄ and TiO₂, confirming the formation of the hybrid

structure. The presence of weak TiO₂ peaks and stronger g-C₃N₄ peaks suggest that a higher composition of g-C₃N₄ is present in the TiO₂-g-C₃N₄. This is well supported by the TGA curves shown in Figure D5.1, where the composition of g-C₃N₄/TiO₂ was determined to be 79.5% of g-C₃N₄ and 20.5% of TiO₂. The derivation of elemental composition from TGA curves can be found in Table D5.1.

UV-Vis diffuse reflectance spectroscopy is employed to study the optical properties of the samples, and the results are presented in Figure 5.3b. When compared with TiO₂, whose absorption is restricted to the UV region, the absorptions of g-C₃N₄ and TiO₂-g-C₃N₄ are red-shifted with a noticeable shoulder in the region between 460 and 560 nm. The optical band gaps of the samples, shown in Figure 5.3c, were estimated using Tauc and Davis–Mott method according to Equation 5.3:

$$(\alpha h\nu)^{\frac{1}{2}} = A(h\nu - E_g) \quad (5.3)$$

where α is the coefficient of absorption, E_g is the band gap, ν is the frequency of radiation, h is Planck's constant, and A is the proportionality constant. TiO₂ has an absorption edge at 393.6 nm with a band gap of 3.15 eV. The band gap of g-C₃N₄ was 2.77 eV, corresponding to an absorption edge at 447.6 nm. The absorption edge of the hybrid TiO₂-g-C₃N₄ extends into the visible region with a band gap of 2.71 eV, corresponding to an absorption edge of 457.6 nm, which is lower than that of TiO₂ by 0.44 eV. The narrower band gap and stronger absorption at longer wavelengths of the hybrid sample are essential for photoexcitation by visible light irradiation.

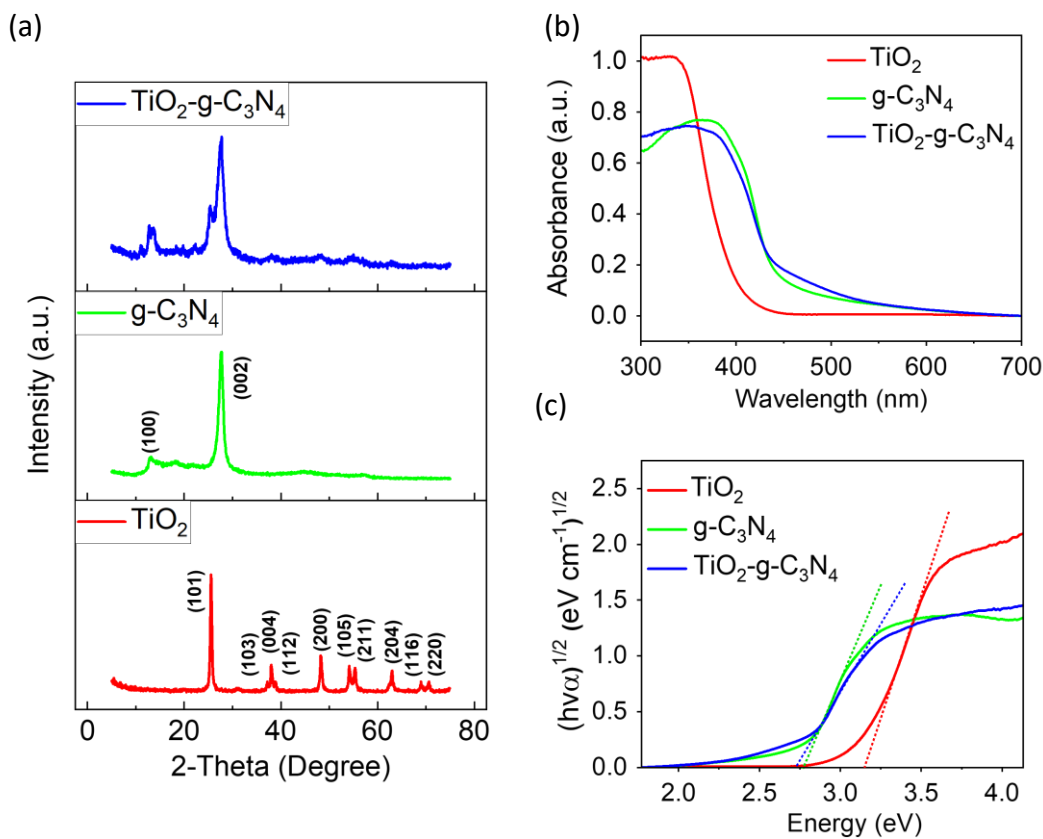


Figure 5.3 (a) X-ray diffraction patterns of TiO_2 , $\text{g-C}_3\text{N}_4$, and $\text{TiO}_2\text{-g-C}_3\text{N}_4$; (b) UV-Vis diffuse reflectance spectra of TiO_2 , $\text{g-C}_3\text{N}_4$, and $\text{TiO}_2\text{-g-C}_3\text{N}_4$; (c) Tauc plots from UV-Vis spectra shown in (b) of TiO_2 (band gap: 3.15 eV), $\text{g-C}_3\text{N}_4$ (band gap: 2.77 eV), and $\text{TiO}_2\text{-g-C}_3\text{N}_4$ (band gap: 2.71 eV).

PL spectroscopy was used to investigate the samples' fluorescence, and the results are shown in Figure 5.4. The samples were excited by different wavelengths (460, 480, 500, 520, 540, and 560 nm). We chose these wavelengths to verify the UV-Vis data (Figures 5.3b and c) that indicate the ability of $\text{g-C}_3\text{N}_4$ and $\text{TiO}_2\text{-g-C}_3\text{N}_4$ to absorb light in the region between 460 and 560 nm. As shown in Figure 5.4b, the $\text{g-C}_3\text{N}_4$ showed high fluorescence in this region, unlike TiO_2 with limited absorption (Figure 5.4a). This observation confirms the generation of charge carriers on $\text{g-C}_3\text{N}_4$ under visible light exposure. $\text{TiO}_2\text{-g-C}_3\text{N}_4$ exhibited a slightly lower fluorescence intensity than $\text{g-C}_3\text{N}_4$ (Figure 5.4c). Because the fluorescence is generated from electron-hole

recombination, the reduction in its intensity indicates the separation of the charge carriers through the Z-scheme junction formed between TiO_2 and $\text{g-C}_3\text{N}_4$.

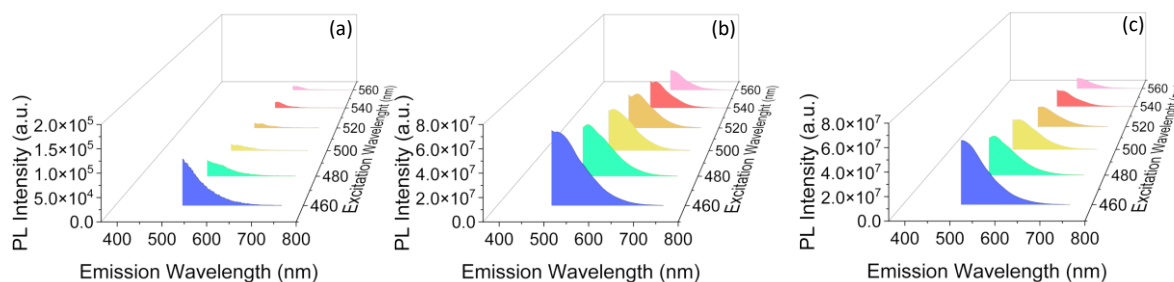


Figure 5.4 Photoluminescence spectra of TiO_2 (a), $\text{g-C}_3\text{N}_4$ (b), and $\text{TiO}_2\text{-g-C}_3\text{N}_4$ (c) hybrids using lights of various wavelengths.

XPS analysis was carried out to investigate the surface chemistry of the samples. Figure D5.2 shows the survey spectra of the photocatalysts. Table D5.2 summarizes the atomic concentration (at%) calculated from the survey spectra. The high-resolution spectra of C 1s, N 1s, and Ti 2p are shown in Figure D5.3. The carbon signal in TiO_2 is attributed to the adventitious carbon (Figure D5.3a). The peaks at 284.8 eV, 286.5 eV, and 288.3 eV in the deconvoluted C 1s spectrum of $\text{g-C}_3\text{N}_4$ correspond to the C-C bond from graphitic carbon residues, C-NH₂ and C=N-C from $\text{g-C}_3\text{N}_4$ backbone, respectively [34, 35]. Similarly, the $\text{TiO}_2\text{-g-C}_3\text{N}_4$ was fitted into three peaks at 284.8 eV, 286.4 eV, and 288.2 eV, confirming the presence of $\text{g-C}_3\text{N}_4$ in the hybrid catalyst. Figure D5.3b shows the high-resolution N 1s spectrum of the samples. The TiO_2 has ~0.9 at% of N in the sample, which may be attributed to the surface-adsorbed nitrogen species from the atmosphere. The N 1s spectra of the $\text{g-C}_3\text{N}_4$ and $\text{TiO}_2\text{-g-C}_3\text{N}_4$ samples were deconvoluted into two peaks at 398.7 eV and 400.2 eV, corresponding to the sp^2 hybridized pyridinic nitrogen (C=N-C) and tertiary nitrogen (N-C₃) confirming the structure of $\text{g-C}_3\text{N}_4$ [34]. There was a third peak located

at 404.5 eV which could be due to the features of amino functional groups with hydrogen on the g-C₃N₄ [36]. Figure D5.3c shows the Ti 2p high-resolution peaks of TiO₂, g-C₃N₄, and the hybrid TiO₂-g-C₃N₄ samples. The Ti 2p spectra of both TiO₂ and TiO₂-g-C₃N₄ samples were deconvoluted into a pair of peaks at binding energies of 458.7 and 464.4 eV, ascribed to the Ti 2p_{3/2} and Ti 2p_{1/2} doublet of Ti⁴⁺ states ascribed to TiO₂ [37].

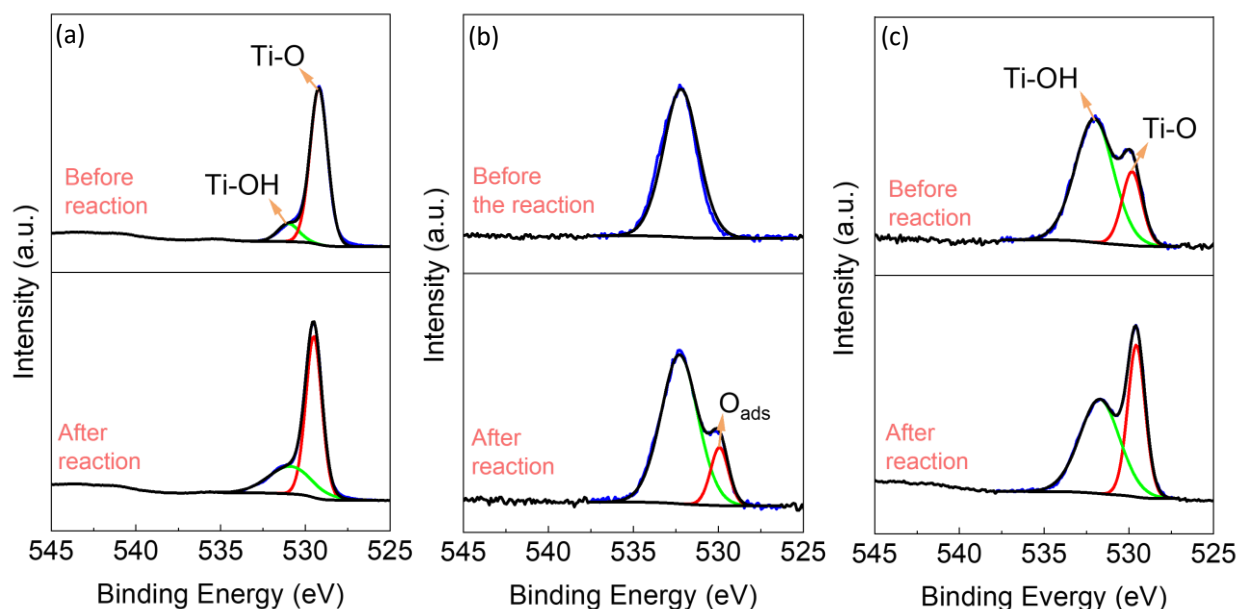


Figure 5.5 High-resolution O1s XPS spectra of TiO₂ (a), g-C₃N₄ (b), and TiO₂-g-C₃N₄ (c) before (top) and after (bottom) the photocatalytic reaction.

High-resolution XPS O1s spectra of TiO₂, g-C₃N₄, and TiO₂-g-C₃N₄ before and after photocatalytic reactions are shown in Figure 5.5. TiO₂ spectrum before the reaction (Figure 5.5a; top) was deconvoluted into two peaks at the binding energy (BE) of 529.2 and 531.1 eV corresponding to Ti-O and Ti-OH, respectively [38]. g-C₃N₄ spectrum before the reaction (Figure 5.5b; top) showed the presence of a dominant peak at 532.2 eV attributed to surface-adsorbed H₂O. The detection of molecularly adsorbed H₂O on g-C₃N₄ by XPS is supported by the findings of previous studies [39-42]. However, few other studies, in contrary, attributed this peak to

chemisorbed oxygen on the g-C₃N₄ surface [43, 44]. TiO₂-g-C₃N₄ spectrum before the reaction (Figure 5.5c; top) was deconvoluted into two peaks located at 529.9 eV and 532 eV attributed to Ti-O and Ti-OH, respectively [45]. The presence of -OH groups on the catalyst surface is essential for trapping the photoexcited charge carriers (particularly the holes) and subsequently forming active radicals for NO_x oxidation; we shall discuss this phenomenon in detail later.

Further characterization of the composite was done by Raman spectroscopy using a 780 nm laser (Figure D5.4). Notably, g-C₃N₄ has a strong fluorescence background mixed in the Raman spectra even using a 780 nm laser; however, characteristic peaks corresponding to g-C₃N₄ and TiO₂ can still be observed on top of the high background. TiO₂ has bands at 141 cm⁻¹ (E_g), 194 cm⁻¹ (E_g), 394 cm⁻¹ (B_{1g}), 513 cm⁻¹ (A_{1g}, B_{1g}), and 637 cm⁻¹ (E_g), characteristic of the anatase phase [46, 47]. The phase composition is consistent with XRD data showing only the anatase phase. The g-C₃N₄ showed bands at 748 cm⁻¹, 1115 cm⁻¹, 1152 cm⁻¹, 1232 cm⁻¹, and 1308 cm⁻¹ corresponding to stretching vibration modes of C-N, characteristic of melamine [48]. The bands at 707 cm⁻¹ and 1558 cm⁻¹ can be attributed to the breathing modes of the s-triazine ring and the stretching modes of the C=N bond, respectively [49, 50]. In the Raman spectra of TiO₂-g-C₃N₄ composite material, Raman bands corresponding to both TiO₂ and g-C₃N₄ could be observed, indicating the presence of both TiO₂ and g-C₃N₄. The E_g vibrational mode of anatase phase TiO₂ was shifted to higher wavenumbers by 6 cm⁻¹ in the composite, which could be due to strain induced by the coating of g-C₃N₄, indicating a stronger interaction between g-C₃N₄ and TiO₂ and/or C, N doping in TiO₂ [51].

5.4 NO_x Photocatalytic Activity

Figure 5.6a shows the NO conversion of TiO₂, g-C₃N₄, and TiO₂-g-C₃N₄ under simultaneous exposure to blue and green light and at 50% RH. NO conversion of TiO₂-g-C₃N₄ is

34 %, four times higher than TiO_2 (7 %) and two times higher than $\text{g-C}_3\text{N}_4$ (17 %). This indicates that coupling TiO_2 with $\text{g-C}_3\text{N}_4$ fosters NO conversion of $\text{g-C}_3\text{N}_4$. Photocatalytic NO_x oxidation typically involves the formation of NO_2 , a more toxic compound than NO; therefore, an effective photocatalyst should minimize the release of NO_2 into the atmosphere while maintaining reasonable conversion of NO. In other words, NO_x oxidation photocatalysts should oxidize NO to NO_2 and then store a significant portion of the formed NO_2 on the surface of the catalyst as nontoxic NO_3^- . Hence, the activity of a photocatalyst in NO_x oxidation should be evaluated by considering both NO conversion and NO_x storage selectivity. De NO_x index, a parameter that measures the overall activity of a photocatalyst in NO_x removal by considering both NO conversion and NO_x storage selectivity, is used to quantify the performance of TiO_2 , $\text{g-C}_3\text{N}_4$, and $\text{TiO}_2\text{-g-C}_3\text{N}_4$. This index was first suggested by Bloch et al.[4], and is based on the assumption that the total toxicity of air is affected three times more by NO_2 than NO. A photocatalyst demonstrates a NO_x “purification effect” when it possesses a positive De NO_x index and hence is preferred. On the other hand, a photocatalyst shows a NO_x “toxification effect” when it has a negative De NO_x index and therefore is undesired.

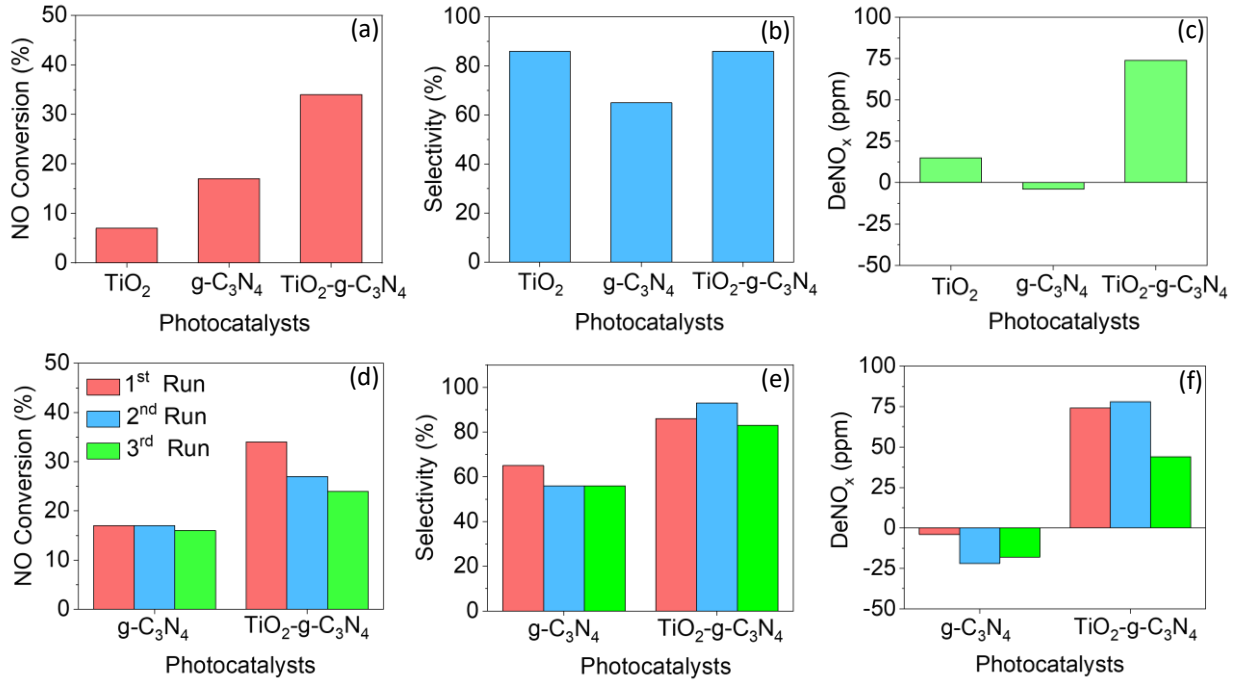


Figure 5.6 Photocatalytic oxidation of NO_x using TiO₂, g-C₃N₄, and TiO₂-g-C₃N₄ under cyan light and 50% RH: (a) NO conversion, (b) NO_x storage selectivity, and (c) DeNO_x index. NO_x oxidation using the recycled g-C₃N₄ and TiO₂-g-C₃N₄ photocatalysts (three consecutive cycles): (d) NO conversion, (e) NO_x storage selectivity, and (f) DeNO_x index.

The DeNO_x index and NO_x storage selectivity of the photocatalysts were calculated by using Equations 5.4, 5.5, and 5.6 [4].

$$\xi = \frac{(c_d - c_i)\dot{V}p}{\varphi ART} \quad (5.4)$$

$$\text{Selectivity} = \frac{\xi_{NO_x}}{\xi_{NO}} \quad (5.5)$$

$$DeNO_x \text{ index} = \xi_{NO_x} \left(3 - \frac{2}{S} \right) \quad (5.6)$$

where ξ is the photonic efficiency of NO_x species; c_d is the species concentrations in dark (ppm); c_i is the species concentrations under illumination (ppm); $\dot{V}$ is the volumetric flow rate; p is the pressure in the system (1 atm); φ is the photon flux at photocatalyst surface (photon/m² s;

dependent on light wavelength and intensity); A is the catalyst irradiated area; R is the gas constant; and T is the temperature.

TiO₂-g-C₃N₄ has a purification effect as it exhibits high NO_x storage selectivity, reasonable NO conversion (34 %), and a positive DeNO_x index (Figures 5.6 b and c); it is therefore suitable for NO_x oxidation. In contrast, g-C₃N₄ exhibited a lower selectivity towards NO_x storage and a negative DeNO_x index (Figure 5.6b and c) with low NO conversion (17 %) as shown in Figure 5.6a, indicating its toxification effect and its unfeasibility for NO_x oxidation. It is noted that although TiO₂ showed a slightly positive DeNO_x index and high NO_x storage selectivity (Figures 5.6b and c), it suffered from very low NO conversion (7 %), confirming its ineffectiveness as a NO_x oxidation photocatalyst.

To evaluate the reusability and long-term activity of the photocatalysts, we conducted three consecutive photocatalytic NO_x oxidation experiments using g-C₃N₄ and TiO₂-g-C₃N₄, and the results are shown in Figure 5.6. The DeNO_x index and selectivity of recycled TiO₂ are not shown because NO conversion of recycled TiO₂ is approximately zero. The NO conversion of TiO₂-g-C₃N₄ slightly decreased after each cycle (Figure 5.6d), likely because of the accumulation of NO_x photooxidation products on the catalyst surface and consequent consumption of NO_x adsorption sites. Nevertheless, the recycled TiO₂-g-C₃N₄ exhibited high selectivity and positive DeNO_x index (Figures 5.6e and f), maintaining its purification effect. g-C₃N₄ experienced a decrease in selectivity after recycling with an increase in the negativity of its DeNO_x index (Figures 5.6 e and f), indicating the increase in its toxification effect and further affirming its unsuitability for NO_x oxidation. Comparing the performance of TiO₂-g-C₃N₄ with other TiO₂-based photocatalysts in the literature is challenging because of the variation in reactor design and reaction conditions. Nevertheless, to give the reader an idea about the performance of TiO₂-based

photocatalysts in NO_x oxidation, we summarized NO conversion, selectivity, and DeNO_x index along with reaction conditions in Table 5.1. TiO₂-g-C₃N₄ showed a high DeNO_x index and selectivity at low photocatalyst concentration, while demonstrating comparable conversion of NO.

Table 5.1 Performance of state-of-the-art photocatalysts at room temperature and 40-50% relative humidity

Catalyst	Light Wavelength (nm)	Catalyst amount (mg)	Inlet NO (ppm)	NO conversion (%)	Selectivity (%)	DeNO _x (ppm) ¹	DeNO _x ²	Ref.
P25	-	300	8	-	27.8	-3689	-	[4]
FeTi4	315-1050	0.55	0.1	23	63	-	-	[52]
25Ca/Ti	315-400	900	1	46	77	-	0.14	[28]
70Al/Ti	315-400	900	1	42	64	-	-0.03	[28]
mpg-CN500	400-700	200	1	40	83	-	0.20	[53]
Ti _{0.909} W _{0.091} O _{2N_x}	-	300	8	-	90	150	-	[54]
Conventional TiO ₂ -g-C ₃ N ₄	> 400	-	1	20	-	-	0.025	[22]
TiO ₂ -g-C ₃ N ₄	425-515	64	1	35	86	74	0.2	This study

¹DeNO_x index calculated based on the procedure reported in this work.

²Modified DeNO_x index calculated based on the study reported by M. Çağlayan et al. [28].

The difference in the photocatalytic activity of TiO₂, g-C₃N₄, and TiO₂-g-C₃N₄ is explained by examining the mechanism of NO_x oxidation, which is split into three steps [28, 55, 56]: (1) the interaction of light and photocatalyst and the consequent formation of charge carriers (Equation 5.7); (2) the reaction between the formed charge carriers and oxygen-containing molecules (O₂ and H₂O)/hydroxyl groups (-OH) on photocatalyst surface and the resulting generation of reactive oxygen species (ROS) (Equations 5.8-5.10); and (3) the oxidation of NO and NO₂ adsorbed on photocatalyst surface via formed ROS to NO_3^- (Equations 5.11-5.16).



The concentration of ROS formed on the surface of TiO₂ is low due to its large band gap and the subsequent poor formation of charge carriers under visible light as depicted in Figure 7a. We did not observe any significant variation in O1s XPS spectra of TiO₂ obtained before and after the reaction as depicted in Figure 5.5a. This observation implies the weak interaction between TiO₂ and surface oxygen-containing species (-OH groups or adsorbed oxygen), likely due to the absence

of charge carriers. Therefore, TiO_2 showed low NO oxidation activity. Although $\text{g-C}_3\text{N}_4$ has a low band gap and is capable of producing charge carriers under visible light, a significant portion of the carriers undergoes recombination. Therefore, only a small amount of charge carriers remains alive on $\text{g-C}_3\text{N}_4$ to participate in the redox reaction, undermining NO_x oxidation. In addition, the VB edge potential of $\text{g-C}_3\text{N}_4$ (+1.63 eV versus NHE) is less positive than the potential required to oxidize H_2O to $\bullet\text{OH}$ (+2.68 versus NHE) or $-\text{OH}$ to $\bullet\text{OH}$ (+1.99 eV versus NHE). Consequently, the direct formation of $\bullet\text{OH}$ on $\text{g-C}_3\text{N}_4$ is improbable. In fact, the presence of a dominant peak attributed to the adsorbed H_2O in the $\text{O}1\text{s}$ XPS spectrum of $\text{g-C}_3\text{N}_4$ collected after the reaction (Figure 5.5b) indicates the weak interaction between the holes and H_2O . In other words, the H_2O adsorbed on $\text{g-C}_3\text{N}_4$ was not consumed by the holes during the reaction. On the other hand, $\text{O}1\text{s}$ XPS spectrum of $\text{g-C}_3\text{N}_4$ obtained after the reaction (Figure 5.5b) detects the presence of a peak at 530 eV associated with the adsorbed oxygen [57], likely formed as a result of electron transfer to O_2 . Hence, the NO_x oxidation will be mainly dominated by $\bullet\text{O}_2^-$, or the so-called electron-mediated mechanism (Equations 5.10, 5.11, 5.14, and 5.15). Although a recent study suggests that the $\bullet\text{O}_2^-$ is crucial to NO_x oxidation through direct conversion of NO to $\text{NO}_3^-/\text{HNO}_3$ [27], this mechanism does not seem proper for $\text{g-C}_3\text{N}_4$, evident by its negative DeNO_x index. It is important to mention that the formation of $\bullet\text{OH}$ cannot be entirely eliminated as there is another pathway for the indirect formation of $\bullet\text{OH}$. This pathway includes the disproportionation of $\bullet\text{O}_2^-$ as depicted in equations (5.17-5.20). The photocatalytic mechanism and electron-mediated mechanism of NO_x oxidation by $\text{g-C}_3\text{N}_4$ are shown in Figures 5.7b and d, respectively. However, the low concentration of $\bullet\text{O}_2^-$ formed on $\text{g-C}_3\text{N}_4$ due to electron-hole recombination undermines its ability to generate a decent amount of $\bullet\text{OH}$ required for effective NO_x abatement. Furthermore, previous studies suggested that NO_x species are only weakly adsorbed on $\text{g-C}_3\text{N}_4$ [21, 22], hindering the first

step in the photocatalytic reaction (adsorption). Therefore, we conclude that the poor NO_x oxidation activity of g-C₃N₄ is due to its low photonic efficiency and poor adsorption capacity.



In the case of TiO₂-g-C₃N₄, the Z-scheme synergy between g-C₃N₄ and TiO₂ allows the migration of photogenerated electrons from TiO₂ CB to recombine with the photogenerated holes in g-C₃N₄ VB. This gives rise to the accumulation of electrons in CB of g-C₃N₄ and holes in VB (or inter-band states) of carbon- or nitrogen-doped TiO₂; thereby, electron-hole separation as depicted in Figure 5.7c. It is noted that TiO₂ in TiO₂-g-C₃N₄ is visible light active due to the presence of inter-band states formed due to carbon and nitrogen doping, as demonstrated previously [15]. CB edge of g-C₃N₄ (-1.17 eV versus NHE) is located above the standard redox potential of O₂/•O₂⁻ (-0.046 eV versus NHE) and CB edge of TiO₂ (-0.31 eV versus NHE) [15]. Therefore, the electrons accumulated in CB of g-C₃N₄ possess higher reducing capability than those in CB of TiO₂ to reduce the adsorbed O₂, favoring the formation of •O₂⁻. The energy levels of carbon or nitrogen impurities in TiO₂ is located at approximately 2.50 eV, which is more positive than g-C₃N₄ VB (+1.63 eV versus NHE) and the potential required to oxidize OH to •OH (+1.99) [15]. Therefore, the energetic holes in TiO₂ can oxidize NO_x through a hole-mediated mechanism (Equations 5.9, 5.12, 5.13 and 5.16), in contrast to g-C₃N₄ in which NO_x oxidation is dominated by electron-mediated mechanism. O1s XPS spectrum of TiO₂-g-C₃N₄ (Figure 5.5c) confirmed the consumption of -OH groups by the energetic holes during the reaction, evident by the reduction in the intensity of peak associated with this species at BE = 532 eV; whereas the increase in the

intensity of peak at BE = ~530 eV can be attributed to O₂ adsorption similar to that of pure g-C₃N₄ in Figure 5.5b. Therefore, TiO₂-g-C₃N₄ is expected to perform NO_x oxidation by both the electron- and hole-mediated mechanisms, leading to the formation of a high concentration of ROS (Figure 5.7c and e). In addition, the unique structure of TiO₂-g-C₃N₄ represented by the presence of macro/mesopores (as confirmed by N₂ adsorption-desorption isotherms) provides a suitable structure for the storage of NO_x oxidation products on the catalyst surface, in contrast to g-C₃N₄. Hence, effective NO_x oxidation is achieved.

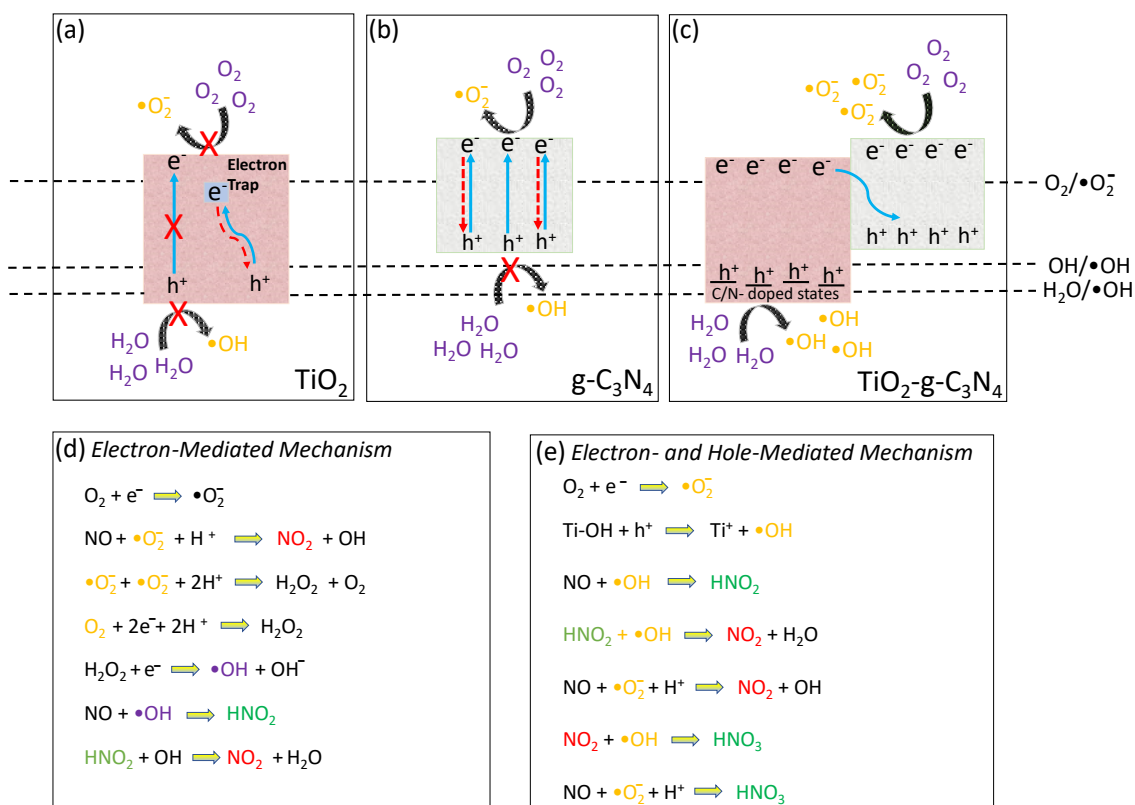


Figure 5.7 Schematic diagram of photo-induced charge carrier formation and subsequent active radicals formed in (a) TiO₂, (b) g-C₃N₄, and (c) TiO₂-g-C₃N₄ under cyan light. Schematic diagrams of (d) an electron-mediated mechanism and (e) a hole-mediated mechanism of NO_x photocatalytic oxidation.

To investigate the impact of water adsorption on NO_x photocatalytic oxidation, we conducted further experiments at low humidity (10% RH). Figures 5.8a, b, and c show concentration profiles of NO_x during the photocatalytic reaction by TiO₂, g-C₃N₄, and TiO₂-g-C₃N₄ under low and high humidity levels. For proper comparison, the experiments were conducted under blue light to eliminate the impact of catalyst photonic efficiency (ability to form charge carriers), as all catalysts are active under blue light. Under low humidity, we did not observe any significant formation of NO₂ by all photocatalysts; NO₂ concentration is almost 0 ppm. TiO₂ and TiO₂-g-C₃N₄ showed approximately identical NO conversion under low humidity, which is remarkably higher than that of g-C₃N₄. However, under high humidity, the NO conversion activity of TiO₂ significantly declined. It may be ascribed to the formation of bridging hydroxyl groups as a result of the dissociation of water molecules on oxygen vacancies of TiO₂ [20, 28]. These groups can capture the photogenerated electrons, boosting their recombination with holes; hence the number of ROS on TiO₂ is expected to be low, and this could be the reason for the poor NO conversion observed. g-C₃N₄ showed higher NO conversion activity under high humidity than under low humidity, with a slight formation of NO₂. The formation of NO₂ can be attributed to the reduction in the adsorption sites available for NO₂ storage due to H₂O adsorption on g-C₃N₄. Interestingly, TiO₂-g-C₃N₄ showed reasonable NO conversion under high humidity, which is slightly lower than that achieved under low humidity, with a noticeable formation of NO₂. Although water dissociation on TiO₂ is still possible with TiO₂-g-C₃N₄ under high humidity, the photo-generated electrons are not trapped by the generated bridging hydroxyl groups but transferred to g-C₃N₄ as explained earlier, leaving holes on TiO₂ for photocatalytic NO_x oxidation. This indicates that the Z-scheme is vital in enabling both electrons and holes to participate in the photocatalytic reaction, and hinders charge carrier consumption by water-induced charge carrier recombination centers.

The increase in the formation of NO_2 by $\text{TiO}_2\text{-g-C}_3\text{N}_4$ under high humidity is ascribed to the adsorption of H_2O on the catalyst surface and the consequent reduction in the number of sites available for NO_x storage. In other words, the H_2O occupies the sites available for the adsorption of the generated NO_2 , hindering its oxidation and leading to its release into the atmosphere. Nevertheless, the formation of NO_2 by $\text{TiO}_2\text{-g-C}_3\text{N}_4$ under a humid environment should not prevent its utilization in NO_x oxidation since it has a net purification effect, evidenced by its positive DeNO_x index under blue light (Figure D5.5) and cyan light (Figure 5.6c).

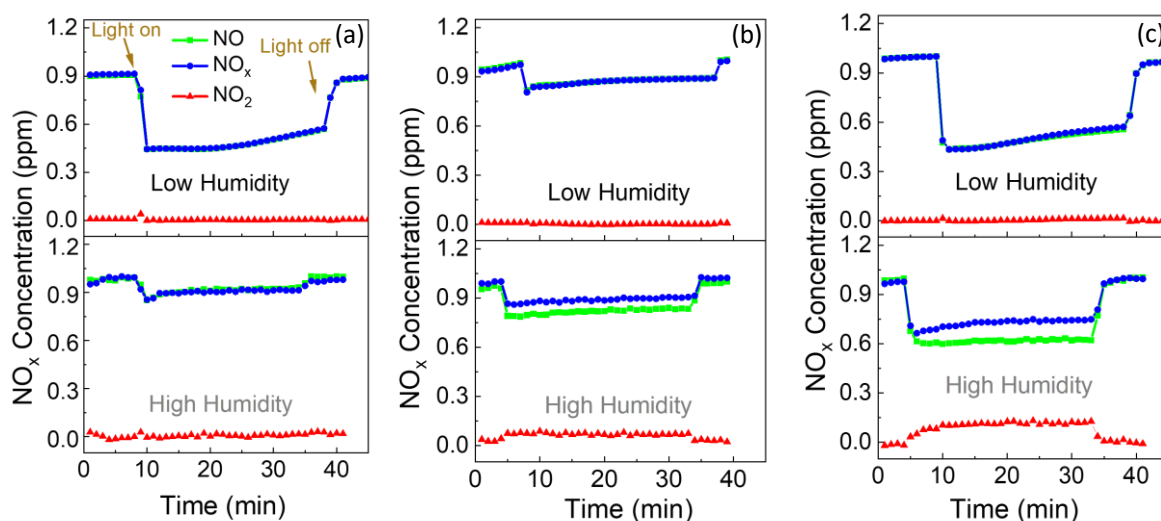


Figure 5.8 Representative NO_x oxidation profiles of TiO_2 (a), $\text{g-C}_3\text{N}_4$ (b), and $\text{TiO}_2\text{-g-C}_3\text{N}_4$ (c) under low and high humidity levels and exposure to blue light.

5.5 Conclusions

A hierarchical macro-mesoporous structure composed of Z-scheme $\text{TiO}_2\text{-g-C}_3\text{N}_4$ hybrid embedded in parallel TiO_2 channels was synthesized and used in photocatalytic NO_x oxidation. The Z-scheme heterojunction formed between TiO_2 and $\text{g-C}_3\text{N}_4$ enabled the separation of a large portion of photogenerated charge carriers while maintaining the high reducing power of electrons in $\text{g-C}_3\text{N}_4$ CB and high oxidizing power of holes in TiO_2 VB, making it possible for $\text{TiO}_2\text{-g-C}_3\text{N}_4$

to perform NO_x oxidation under cyan light. TiO₂-g-C₃N₄ showed superior NO conversion than TiO₂ and g-C₃N₄. TiO₂-g-C₃N₄ also showed superior NO_x storage capacity and, in turn, demonstrated a purification effect, in contrast to g-C₃N₄, with a toxification effect and TiO₂, with a limited purification effect. This study revealed the impact of humidity on NO_x oxidation activity of catalysts and proposed possible pathways for the consumption of charge carriers and reduction of NO_x storage sites. Furthermore, detailed photocatalytic mechanisms of NO_x oxidation by g-C₃N₄ and TiO₂-g-C₃N₄ were suggested. The finding of this study is expected to stimulate researchers to utilize hierarchical TiO₂-based hybrid photocatalysts in NO_x oxidation and explore their application in practical NO_x abatement under ambient conditions.

5.6 References

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Chapter 6 - Detonation Synthesis of TiO₂-TiC Shell-Core Hybrids for NO_x Photooxidation

Chapter 6 is reprinted from:

Ahmed Al Mayyahi, Shusil Sigdel, Christopher M. Sorensen, and Placidus B. Amama, Detonation synthesis of shell-core TiO₂-TiC for photocatalytic NO_x oxidation (manuscript in preparation)

TiO₂ absorption can be extended to visible light region by various approaches including metal and non-metal doping, surface reduction, and coupling with a narrow band gap semiconductor. However, the trade-off relationship between light absorption of TiO₂ and its catalytic activity is a significant challenge. Doping or reduction is based on creating localized energy states above or below the valance band or conduction band of TiO₂ [1]. These states allow intra-band transition of electrons under visible light, enabling visible light absorption. However, the concentration of these localized energy states in conventional photocatalysts is low due to the non-uniform interaction between TiO₂ and the dopants. Also, the same localized energy states serve as recombination centers for charge carriers, particularly those formed as a result of TiO₂ reduction, boosting electron-hole recombination [1-3]. While coupling TiO₂ with a narrow band gap semiconductor can enable visible light activity without compromising electron-hole separation as demonstrated in Chapter 5, this approach may reduce photocatalyst stability and undermine its practical application [4].

TiO₂-nanocarbon shell-core structure has recently emerged as promising visible light active photocatalysts [4-6]. In this unique structure, the nanocarbon (the core) shares a few carbon atoms with TiO₂ (the shell) to create localized energy states in its band, enabling electron transition under visible light. At the same time, the nanocarbon may serve as an electron (or a hole) reservoir to accept the electrons (or holes) from TiO₂, hindering charge carrier consumption induced by the

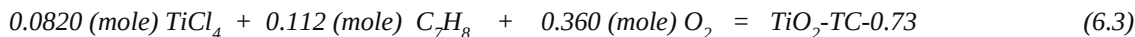
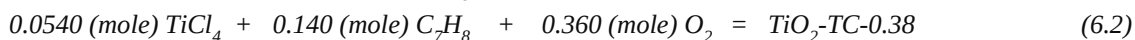
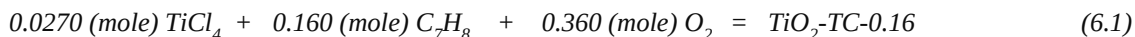
localized energy states. More importantly, the well-tailored boundary between TiO_2 and the nanocarbon at the interface in the shell-core structure maximizes the number of the localized energy states in TiO_2 band and boosts visible light absorption. It is also noted that previous studies showed that a shell-core structure possesses higher stability compared to other binary structures [7].

Among various nanocarbon, TiC is an earth-abundant early transition metal featured by its high electrical conductivity and superior stability under harsh conditions [8, 9]. Nevertheless, TiO_2 -TiC shell-core structure is rarely used in photocatalysis, probably due to the difficulties associated with its synthesis. TiO_2 -TiC shell-core structure is typically produced by thermal nucleation of TiO_2 shell on the surface of commercial TiC [4, 10]. The synthesis of TiC itself is complicated; TiC is commercially synthesized by “the carbothermal reduction” of TiO_2 . The carbothermal reduction is based on a reaction between TiO_2 and carbonaceous source (i.e., carbon black) at high temperature for 10-24 hours [11]. Therefore, the overall synthesis of TiO_2 -TiC shell-core structure is time-consuming and requires complex tools typified by the presence of at least three reactors to synthesize the raw materials (TiO_2 , carbonaceous materials, and TiC). This, in turn, reduces production efficiency and increases synthesis cost. It is also important to mention that controlling the size and morphology of TiO_2 -TiC shell-core structure by the conventional approach is challenging [11]. Due to the versatility of TiO_2 -TiC shell-core structure, as it is not only highly desired in photocatalysis but also in energy storage and conversion [10, 12], an alternative synthesis approach is urgently needed.

In this study, we report a one-step, ultrafast, scalable, economical, and totally new process to synthesize narrow band gap TiO_2 -TiC shell-core structure. Our approach is based on detonating

a mixture of toluene (C₇H₈) and titanium tetrachloride (TiCl₄) with oxygen (O₂) in a multi-liter chamber to produce around seven grams of TiO₂-TiC shell-core structure per second.

To synthesize TiO₂-TiC shell-core structures, a mixture of C₇H₈ (*l*) and TiCl₄ (*l*) is injected into the reactor which is preheated to 80 °C. The mixture is detonated in the presence of oxygen by a spark (10,000 V) formed from an industrial step-up transformer. Various concentrations of C₇H₈ and TiCl₄ are used, while O₂ concentration was maintained at 0.36 mole, as shown in equations (6.1-6.4). The synthesized structures are calcined at 500 °C to remove impurities, and denoted as TiO₂-TiC-X, where X = mole of C₇H₈/mole of TiCl₄.



XRD analysis of the detonation structures is shown in Figure 6.1. All hybrids contain TiC and rutile TiO₂, evident by the presence of peaks at 27.4°, 44°, 54.4°, 56.6°, 62.7°, 64°, and 69° attributed to (110), (210), (211), (220), (002), (310), and (301) facets of rutile [13] and peaks at 36.1° and 41.3° associated with (111) and (200) planes of TiC [14]. The presence of anatase TiO₂ is only observed at C₇H₈/TiCl₄ < 1, evident by the presence of peaks at 25 °, 37.9°, and 48.2° ascribed to (101), (004), and (200) planes of anatase TiO₂ [15]. The results suggest that the ratio of TiCl₄ to C₇H₈ is a crucial factor to regulate TiO₂ phases in the structure. In addition, SEM images of synthesized structures and the corresponding size histograms (Figure E6.1) indicate that this ratio is also essential to control the size and morphology of the samples. XPS analysis (Figure E6.2) of the samples does not detect the presence of peaks associated with TiC, suggesting that

surface of the samples is mainly consisted of TiO_2 , likely due to the formation of shell-core structure.

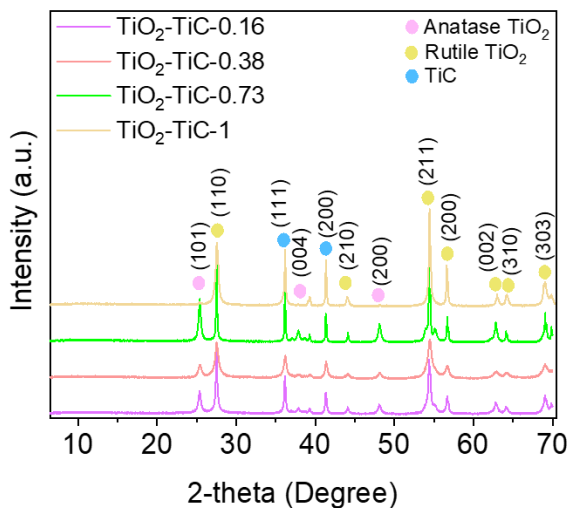


Figure 6.1 XRD pattern of detonation samples.

Compared with P25, the samples exhibit noticeable absorption in the visible light region (Figure 6.2a). Based on the modified Tauc plot approach (Figure 6.2b) [16], the band gaps of TiO_2 -TiC-0.16, TiO_2 -TiC-0.38, TiO_2 -TiC-0.73, and TiO_2 -TiC-1 are estimated to be 3.00, 3.14, 2.93, and 3.06 eV, respectively, which are smaller than that of commercial TiO_2 (P25, 3.25 eV). Since the band gap of TiO_2 -TiC-0.73 is the lowest among the other hybrids, we will focus on this structure hereafter.

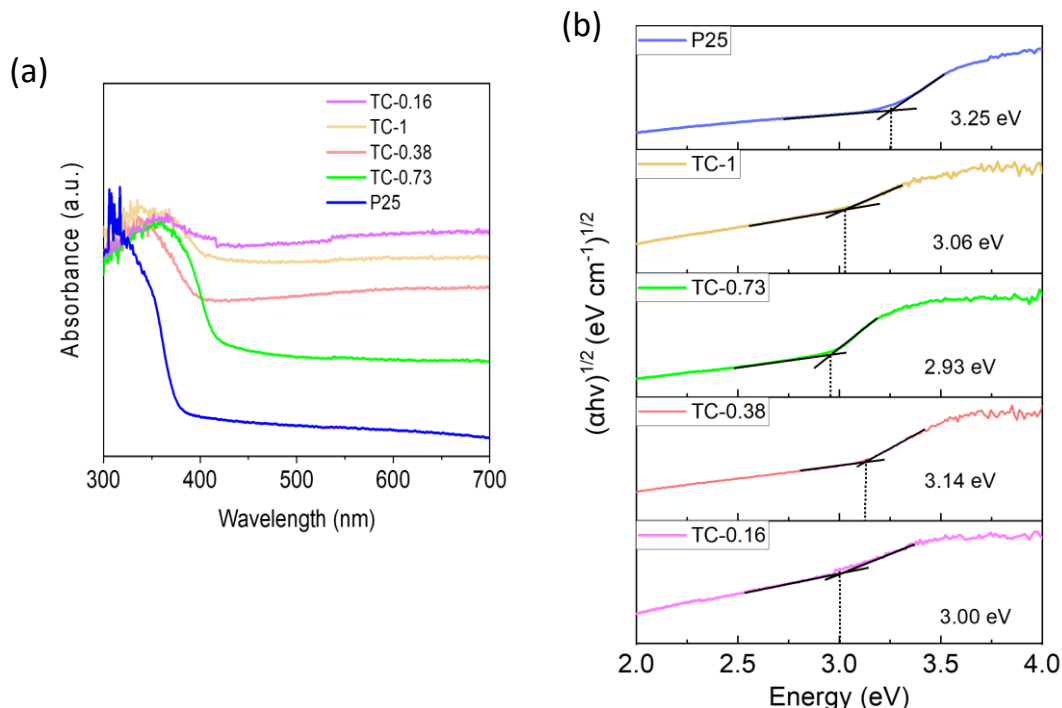


Figure 6.2 (a) UV-Vis measurements and (b) Tauc's plots of detonation samples.

TEM image (Figure 6.3a) of TiO₂-TiC-0.73 confirms the formation of shell-core structure and the high-resolution TEM image (Figure 6.3b) taken on the shell asserts that the shell is made of TiO₂, evident by the presence of dominant lattice fringe corresponding to (011) rutile TiO₂. EDS mapping (Figure 6.3d) and EDS (Figure 6.3e) line scanning detect the presence of a high amount of carbon in the core, suggesting that the TiC is located in the core. While the peaks in XPS spectrum of TiO₂-TiC-0.73 are mainly attributed to TiO₂, as mentioned earlier, peaks associated TiC appear upon etching the sample by argon beam, as depicted in XPS depth profile spectra (Figure 6.4). This further indicates that the TiC is located in the core. Therefore, TEM, EDS, and XPS confirm the formation of TiC core sandwiched by TiO₂ shell by the detonation process.

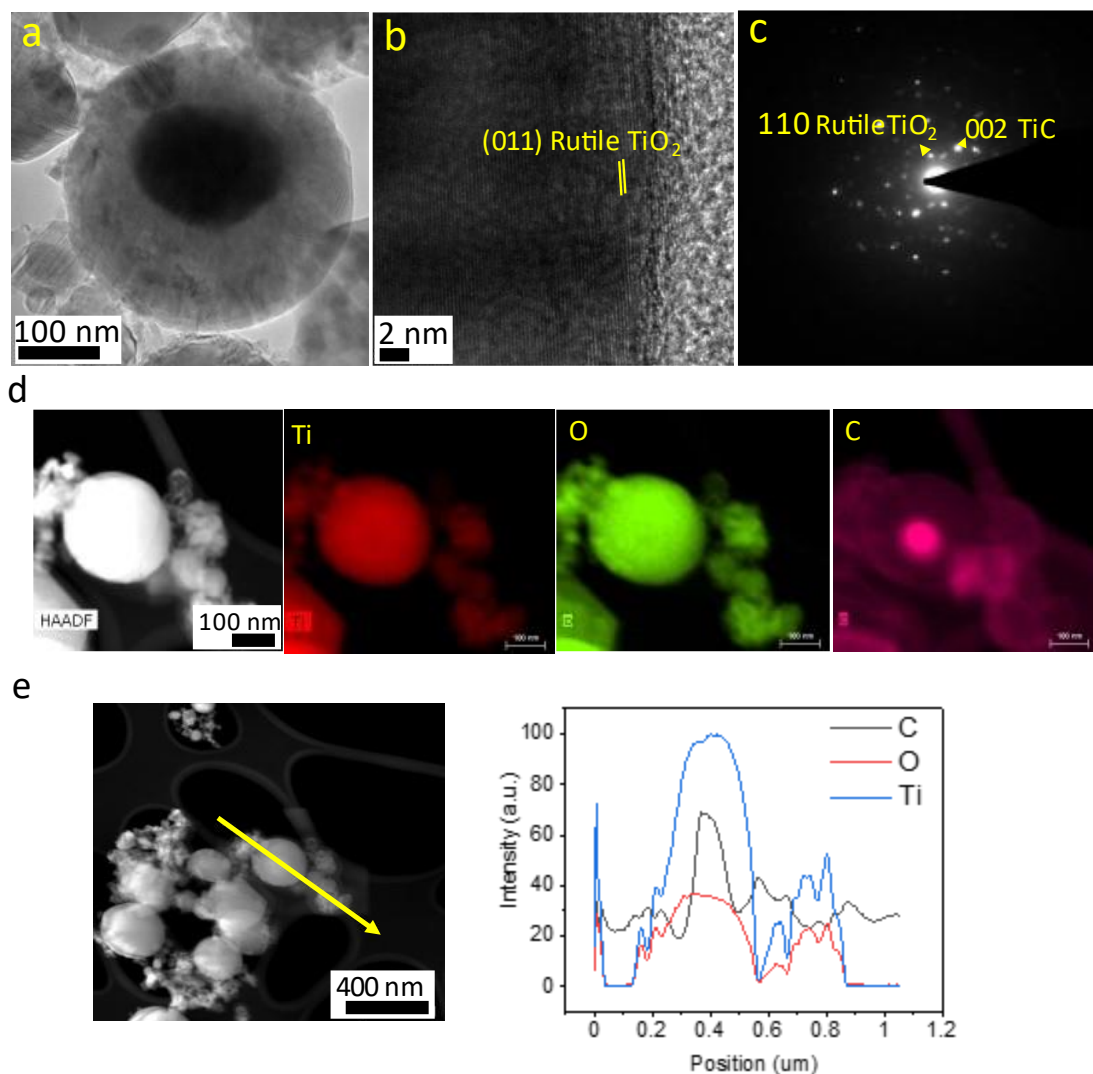


Figure 6.3 Characterization of $\text{TiO}_2\text{-TiC-0.73}$. (a) TEM image of $\text{TiO}_2\text{-TiC-0.73}$, (b) high-resolution TEM image, and (c) selected area electron diffraction (SAED) pattern. (d) SEM image and the corresponding EDS mapping and (e) SEM image and EDS line scan along the yellow arrow in the image.

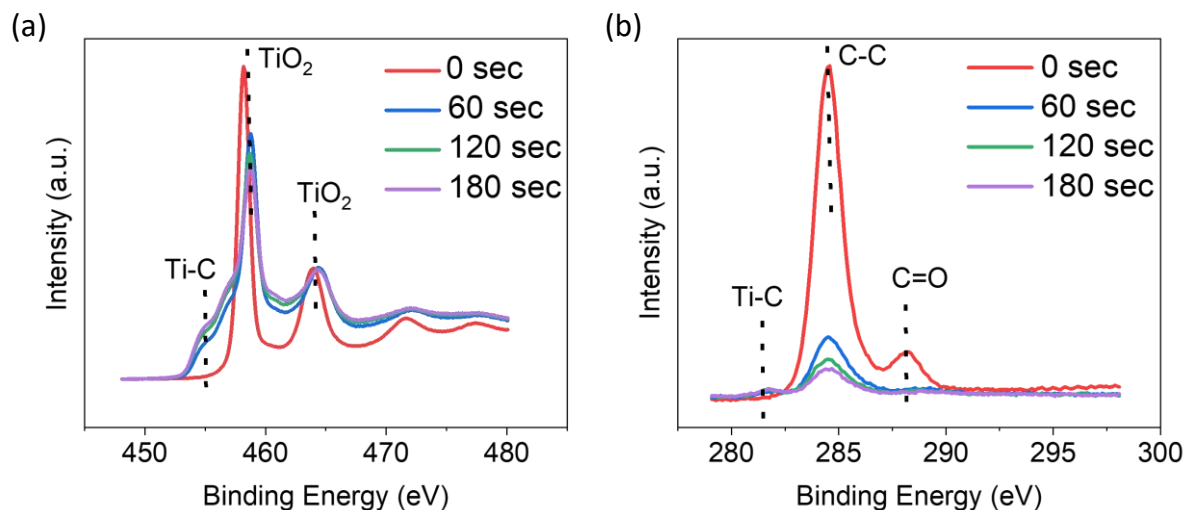


Figure 6.4 XPS depth profile of TiO₂-TiC-0.73 in Ti 2p and C 1s regions.

TiO₂-TiC-0.73 is coated on a glass slide (37.5 cm²) and used in two consecutive runs of NO_x oxidation in a continuous flow reactor. The first run is performed under UV light and the second run is conducted under visible light (blue light), and the results are shown in Figures E6.3 and 6.5. Upon blue light exposure, TiO₂-TC-0.73 shows noticeable NO conversion with a purification effect under low and high humidity levels, confirming the potential of utilizing this structure in visible light driven photocatalysis (Figure 6.5a and b). The NO conversion of TiO₂-TC-0.72 (c.a. 30%) is 3 times higher than that of commercial TiO₂ (c.a. 10 %) as depicted in Figure 6.5c, further confirming the activity of TiO₂-TC-0.73 under visible light. It is noted that under visible light and high humidity, commercial TiO₂ does not generate significant amounts of NO₂, evident by its purification effect (Figure 6.5d). This observation contradicts the characteristic performance of P25 which featured by its toxification effect. Therefore, considering the relatively large band gap of P25 (3.25 eV), it is reasonable to believe that the 10% conversion achieved under visible is due to non-photocatalytic routes. Interestingly, TiO₂-TC-0.73 shows higher NO conversion than P25 under UV light (Figure E6.3). Both P25 and TiO₂-TC-0.72 have more or less

identical surface area, 47.894 m²/g for TiO₂-TiC-0.73 and 58.961 m²/g for P25 (based on BET measurements). Therefore, the difference in the photocatalytic activity of P25 and TiO₂-TiC-0.73 under UV light is attributed to the difference in the concentration of charge carriers on their surfaces, with the likelihood of higher concentration of carriers on TiO₂-TiC-0.73.

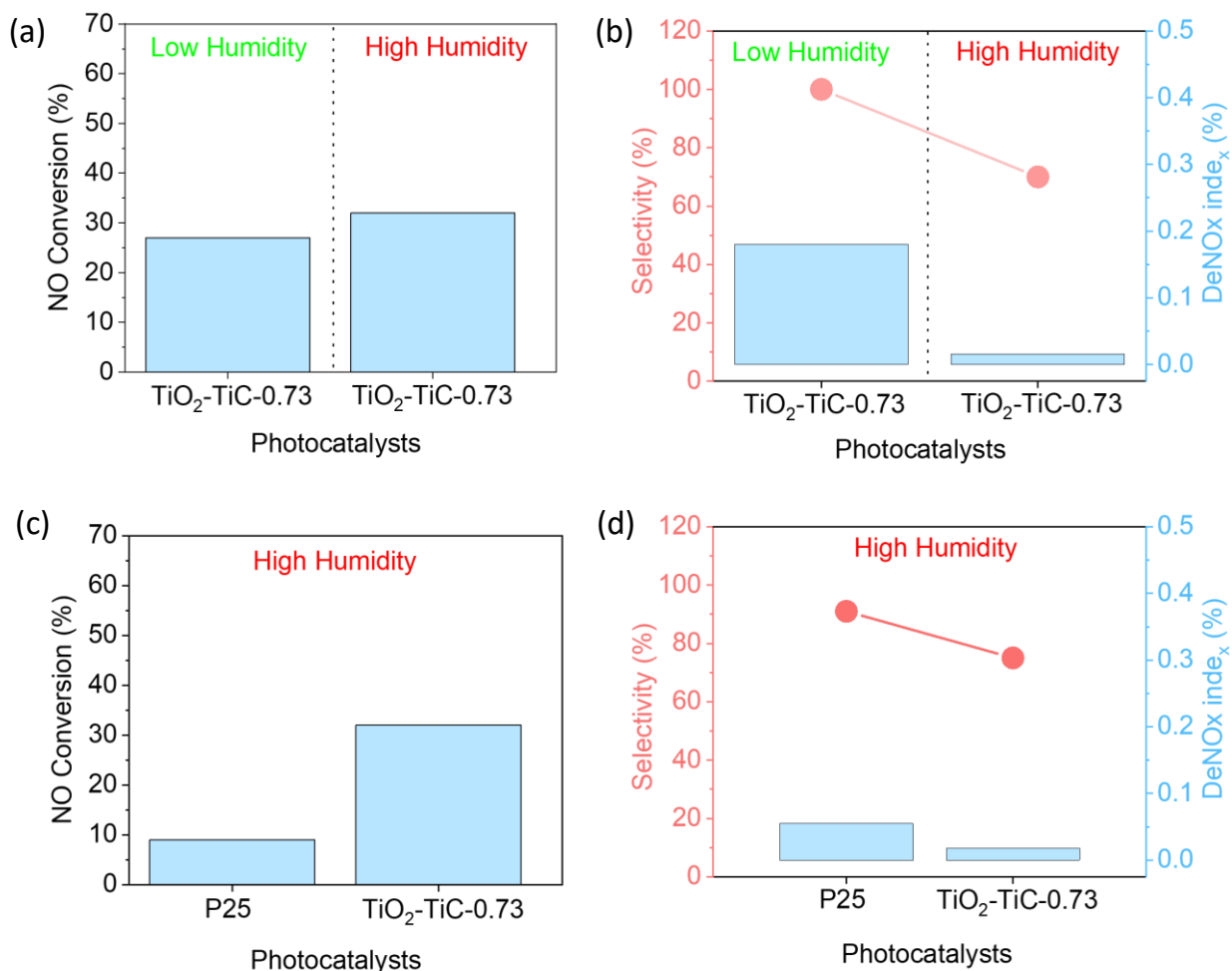


Figure 6.5 (a) NO conversion and (b) DeNO_x index and NO_x storage selectivity of TiO₂-TiC-0.73 under different humidity levels (high and low humidity). (c) NO conversion and (d) DeNO_x index and NO_x storage selectivity of P25 and TiO₂-TiC-0.73 under high humidity.

In TiO₂-TiC-0.73, TiC is expected to accept the electrons from TiO₂, as suggested by another study [4], leaving holes in the shell which are then tarped by H₂O adsorbed on the surface to form hydroxyl radical, enabling the hole-mediated NO_x oxidation. It is noted that TiC is

characterized by strong localized surface plasmon resonance (LSPR) absorption in visible light [17]; hence, it can form hot electrons. These energetic electrons may get ejected from TiC to TiO₂ and then trapped by the oxygen adsorbed at the surface to form superoxide radicals, enabling the electron-mediated NO_x oxidation. The impact of this expected spatial transfer of photoexcited electrons from TiO₂ to TiC and hot electrons from TiC to TiO₂ may favor electron-hole separation. However, further investigation is needed to confirm this phenomenon and its influence on the photocatalytic process. The mechanistic investigation of charge carrier dynamics and NO_x oxidation in TiO₂-TiC shell-core structure will be addressed in a future work.

In summary, we have demonstrated a facile, economical, and scalable approach to synthesize a narrow band gap TiO₂-TiC shell-core structure. Our approach is based on detonating a mixture of TiCl₄ and C₇H₈ in milli-liter reactor to produce 7 grams of the shell-core structure per second. TiO₂-TiC shell-core structure absorbs longer wavelengths than commercial TiO₂ (P25) and performs effective NO_x oxidation under visible light. The finding of this study will allow the versatile TiO₂-nanocarbon shell-core structure to contribute to the materials marketplace and engage in practical applications.

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Chapter 7 - Conclusions

This study demonstrates the coupling of TiO_2 with nanocarbons (CNTs, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, g- C_3N_4 , and TiC) to design photocatalysts with superior activity. The study involves manipulating the chemical and physical properties of the nanocarbons and TiO_2 to enable their effective coupling and adapt the properties of the produced photocatalysts for efficient environmental abatement. The study also presents novel, safe, and cost-effective approaches for scalable synthesis of TiO_2 -nanocarbon photocatalysts. The main findings of this study are summarized below:

- Adapting the size of CNTs to be compatible with that of TiO_2 maximizes the number of junctions formed between them and this, in turn, provides high number of channels for charge carrier transport in TiO_2 -CNT hybrids, leading to effective electron-hole separation and high photocatalytic activity. We show that wrapping short CNTs (125 nm) on TiO_2 nanoparticles (100 nm) leads to superior separation of charge carriers and acetaldehyde oxidation than TiO_2 coupled with long CNTs (1.2 μm).
- Delaminating the MXene and reducing the fluorine-containing groups (increasing oxygen-containing groups) on its surface enables efficient photon- TiO_2 interaction in TiO_2 -nanocarbon photocatalyst and boosts NO_x adsorption on the photocatalyst, respectively.

Two approaches to fabricate delaminated MXene with oxygen-containing groups are demonstrated. The first one depends on intercalating the layers of the conventional MXene with a large size organic molecule (TPAOH) to simultaneously delaminate the layers and reduce the fluorine on their surface. The second relies on etching MAX phase with sodium hydroxide (NaOH) in the presence of a delaminating agent (hydrazine) to form delaminated MXene with high concentration of oxygen-containing groups in one step.

Coupling the delaminated MXene with TiO_2 generates a photocatalyst with high concentration of photoinduced charge carriers without compromising light penetration to TiO_2 . More importantly, the presence of oxygen-containing groups on the MXene surface boosts NO_2 adsorption on photocatalyst surface and hinders its release to the atmosphere, facilitating its subsequent conversion to nitrate. Therefore, a photocatalyst with purification effect is produced.

- Embedding $\text{g-C}_3\text{N}_4$ in a macro-mesoporous structure composed of TiO_2 nanospheres attached to the walls of parallel TiO_2 channels forms a photocatalyst with high adsorption capacity and enables the utilization of $\text{g-C}_3\text{N}_4$ in NO_x oxidation under visible light. TiO_2 - $\text{g-C}_3\text{N}_4$ shows superior NO conversion than TiO_2 and $\text{g-C}_3\text{N}_4$. TiO_2 - $\text{g-C}_3\text{N}_4$ also shows superior NO_x storage capacity and, in turn, demonstrates a purification effect, in contrast to $\text{g-C}_3\text{N}_4$, with a toxification effect, and TiO_2 , with a limited purification effect.
- Detonating a mixture of toluene and titanium tetrachloride in a milli-liter reactor forms a narrow band gap TiO_2 -TiC shell-core photocatalyst. This process is ultrafast, scalable, and cost-effective. The TiO_2 -TiC shell-core photocatalyst demonstrates a notable activity in NO_x oxidation under visible light.

This study provides a deeper understanding of the synthesis of nanocarbons and their role in photocatalytic reactions. It also establishes a rational basis for the design of TiO_2 -nanocarbon hybrid photocatalysts. The knowledge presented in this study is expected to enable the utilization of photocatalysis in practical environmental remediation.

Appendix A - Supplementary Information for Chapter 2

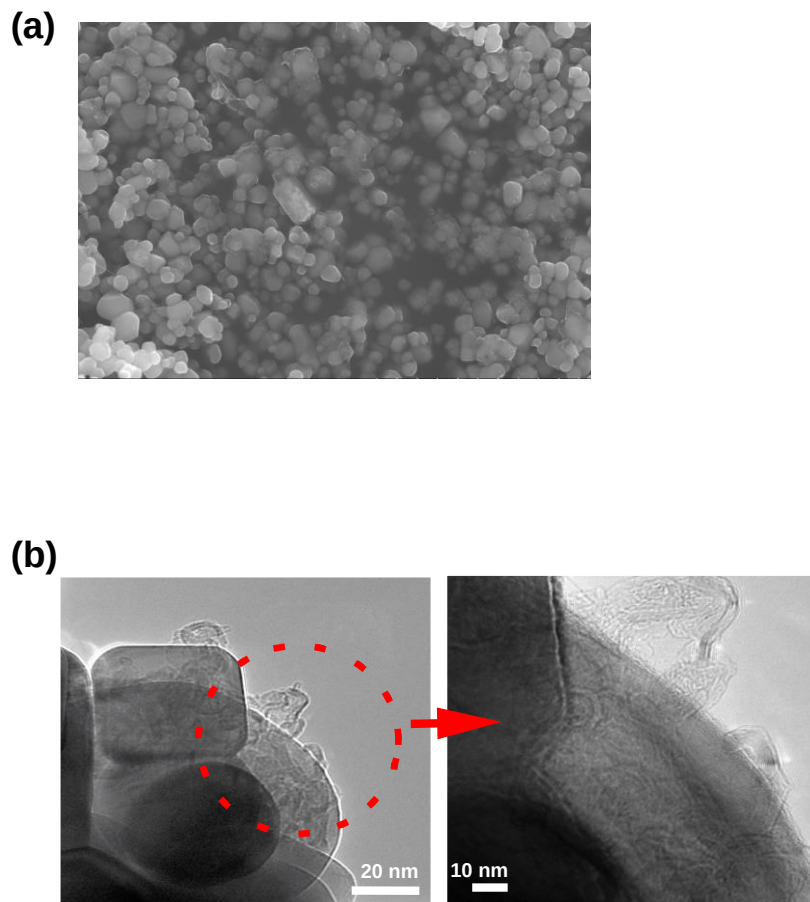
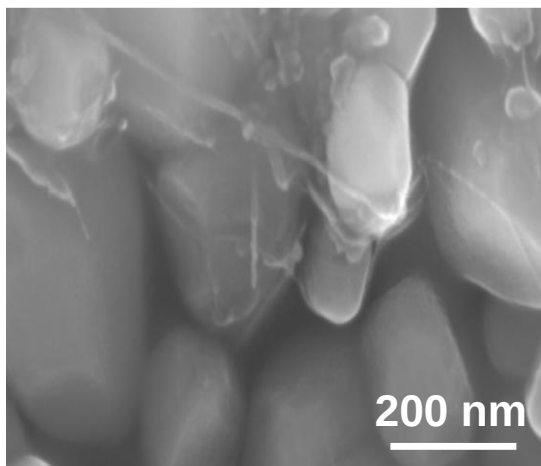


Figure A2.1 (a) SEM image of TiO_2 -short SWCNT and (b) HR-TEM image of TiO_2 -short SWCNT. SWCNT weight ratio is 1 wt. % of TiO_2 . Reprinted from reference [1]. Copyright Royal Society of Chemistry 2021.

(a)



(b)

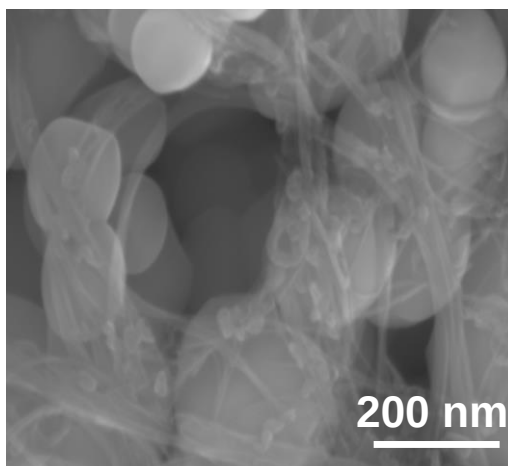


Figure A2.2 SEM images of hybrids with different short SWCNT loading, (a) 1 wt. % and (b) 3 wt. %. Reprinted from reference [1]. Copyright Royal Society of Chemistry 2021.

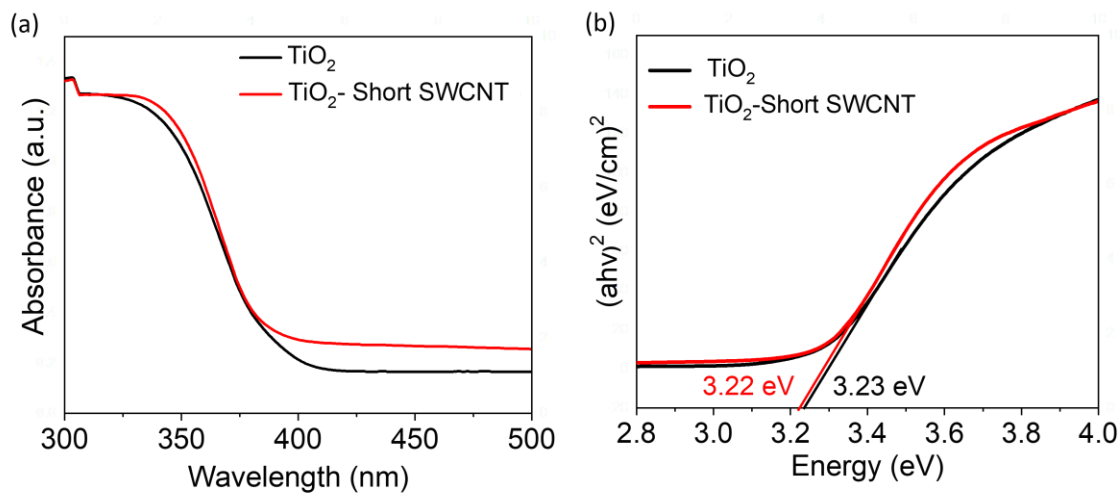


Figure A2.3 (a) UV-Vis spectra of TiO_2 and TiO_2 -short SWCNT (b) Tauc's plot of TiO_2 and TiO_2 -short SWCNT. SWCNT weight ratio is 1 wt. % of TiO_2 . Reprinted from reference [1]. Copyright Royal Society of Chemistry 2021.

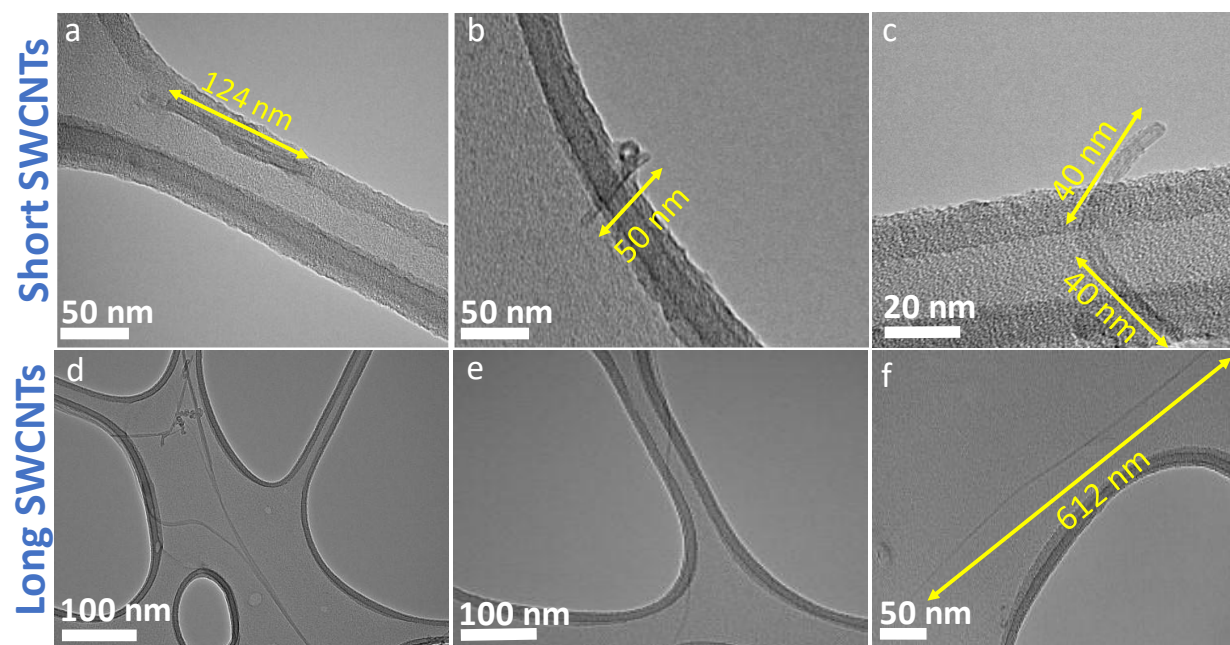


Figure A2.4 Representative TEM images of short SWCNTs (a, b, and c) and long SWCNTs (d, e, and f). Reprinted from reference [1]. Copyright Royal Society of Chemistry 2021.

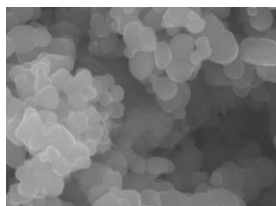


Figure A2.5 SEM image of TiO₂-long SWCNT hybrid. SWCNT weight ratio is 1 wt. % of TiO₂. Reprinted from reference [1]. Copyright Royal Society of Chemistry 2021.

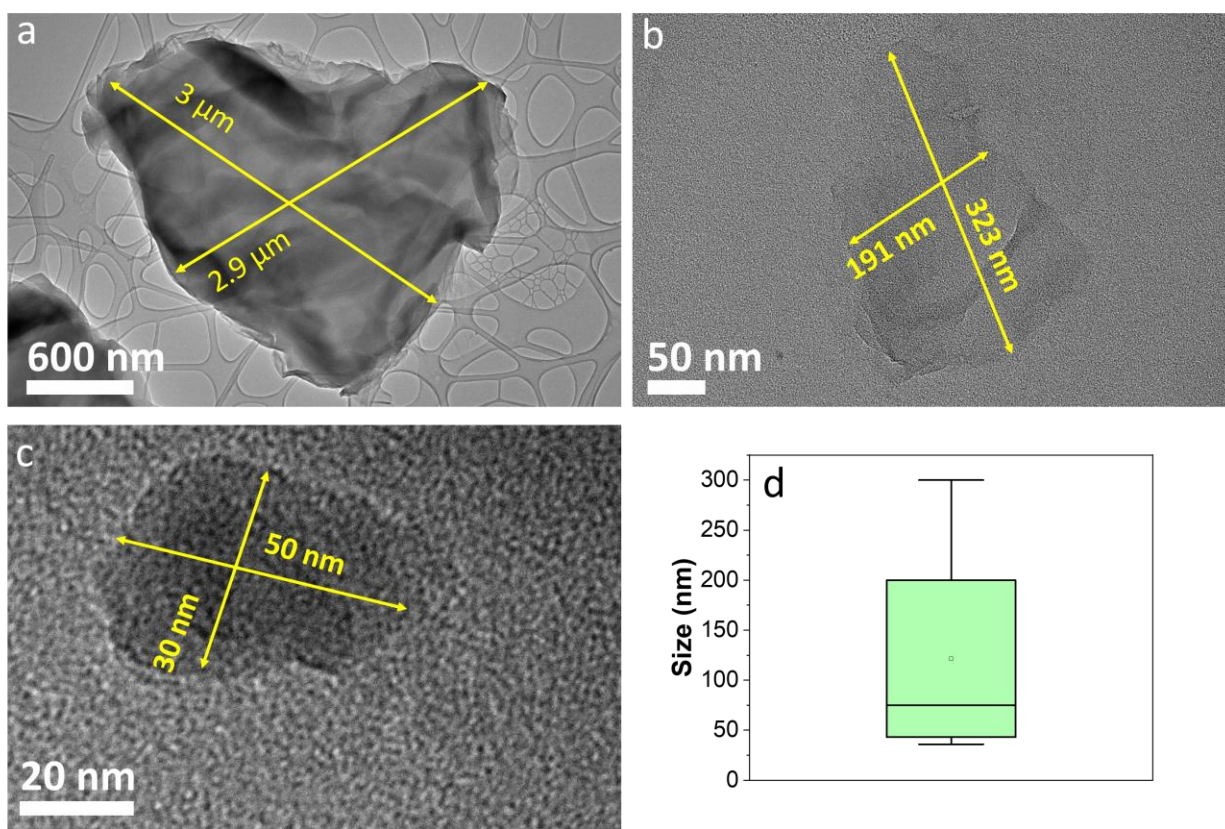


Figure A2.6 TEM images of (a) microsized graphene oxide, (b) exfoliated nanographene oxide, and (c) non-exfoliated nanographene oxide. (d) A box plot of the size of nanographene oxide. Average size is 125 ± 86 nm. Reprinted from reference [1]. Copyright Royal Society of Chemistry 2021.

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Appendix B - Supplementary Information for Chapter 3

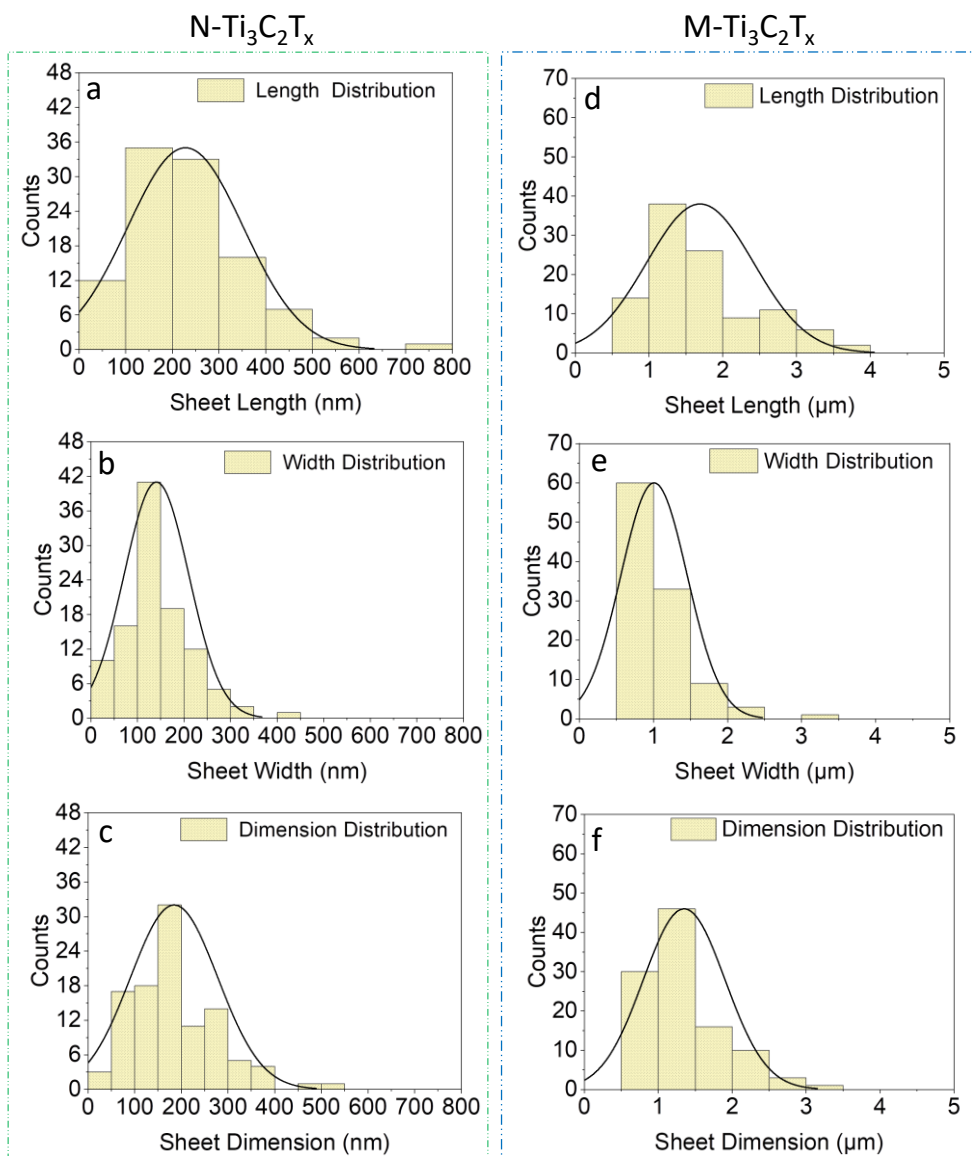


Figure B3.1 Size statistics of MXene sheets. (a) length distribution, (b) width distribution, and (c) dimension (average of length and width) distribution of N-Ti₃C₂T_x. (d) length distribution, (e) width distribution, and (f) dimension (average of length and width) distribution of M-Ti₃C₂T_x. Reproduced from reference [1]. Copyright Elsevier 2022.

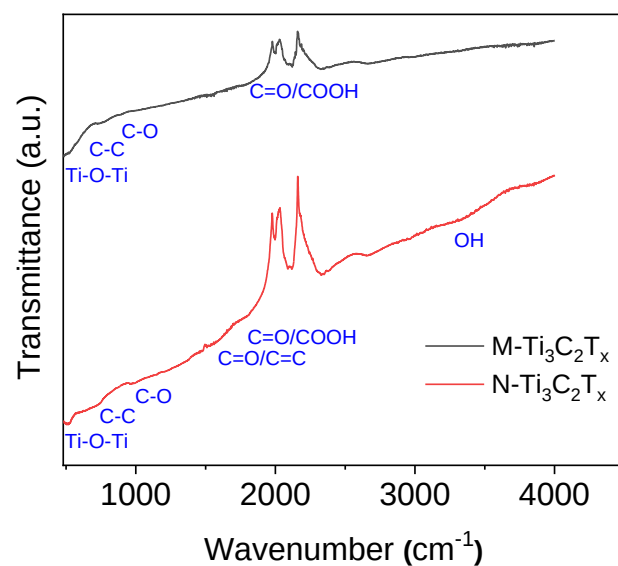


Figure B3.2 FTIR spectra of $\text{M-Ti}_3\text{C}_2\text{T}_x$ and $\text{N-Ti}_3\text{C}_2\text{T}_x$. Reproduced from reference [1]. Copyright Elsevier 2022.

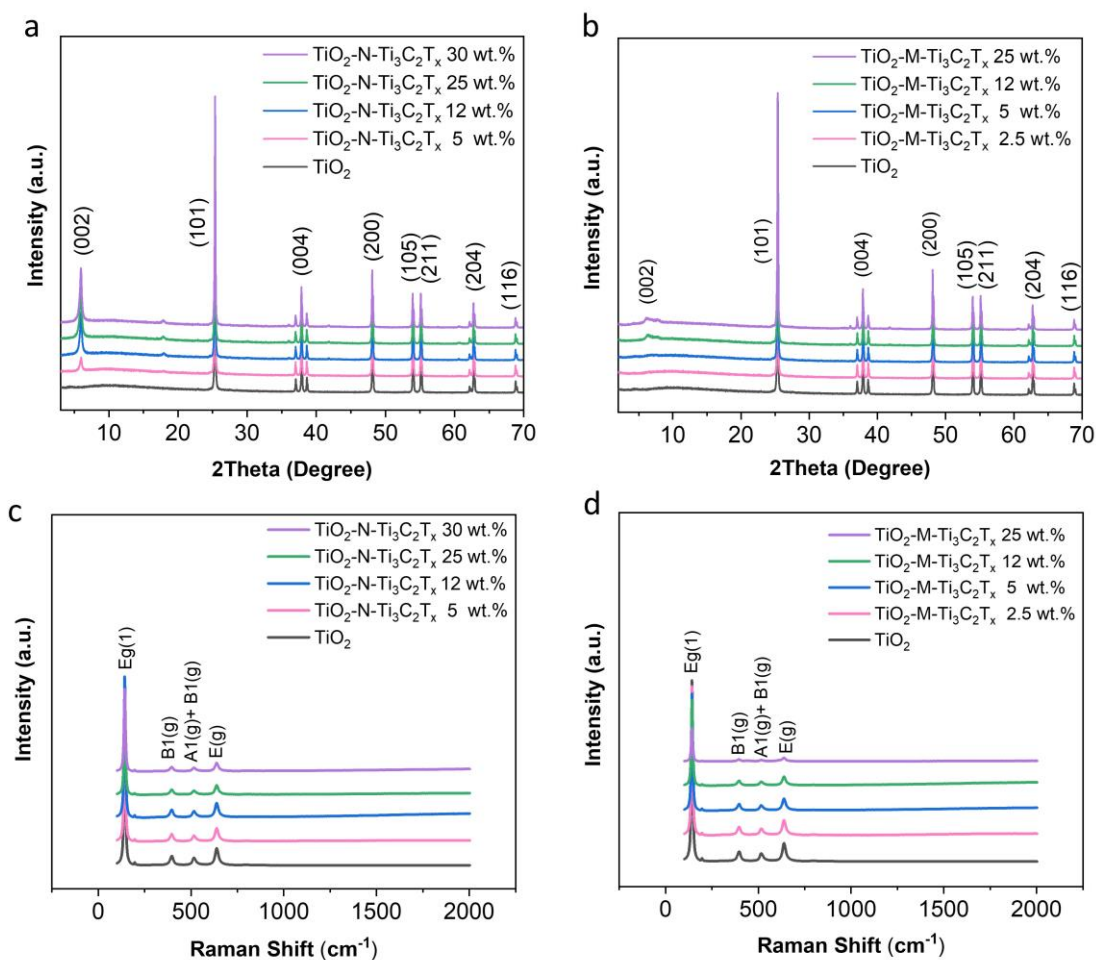


Figure B3.3 XRD spectra of TiO₂-N-Ti₃C₂T_x (a) and TiO₂-M-Ti₃C₂T_x (b) with different amounts of Ti₃C₂T_x. Raman spectra of TiO₂-N-Ti₃C₂T_x (c) and TiO₂-M-Ti₃C₂T_x (d) with different amounts of Ti₃C₂T_x. Reproduced from reference [1]. Copyright Elsevier 2022.

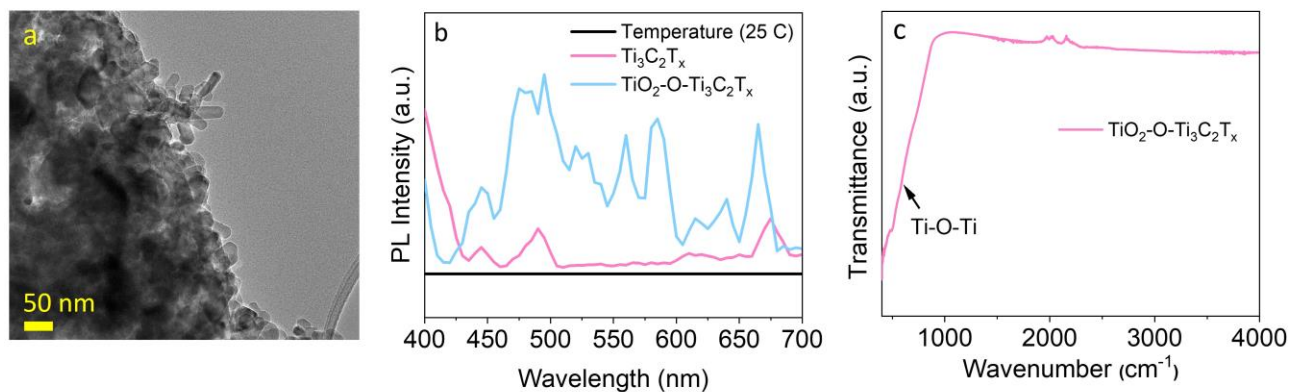


Figure B3.4 TEM image (a), PL spectrum (b), and FTIR spectrum (c) of $\text{TiO}_2\text{-O-Ti}_3\text{C}_2\text{T}_x$. Reproduced from reference [1]. Copyright Elsevier 2022.

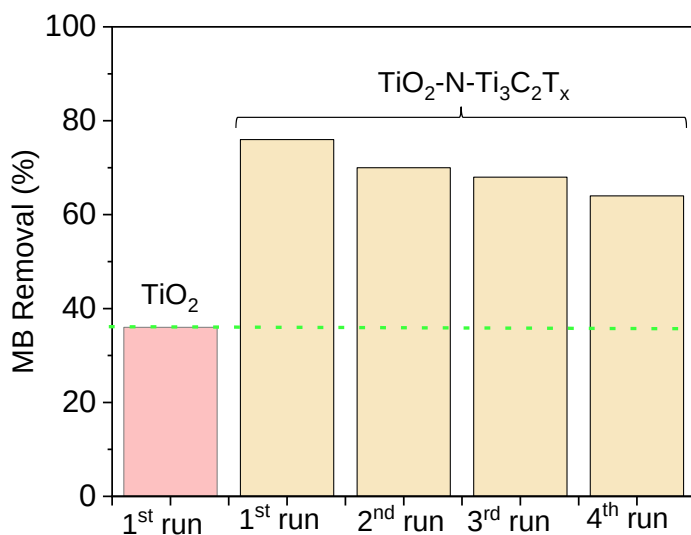


Figure B3.5 MB removal by $\text{TiO}_2\text{-N-Ti}_3\text{C}_2\text{T}_x$ in four photocatalytic cycles, each cycle is 30 minutes. Reproduced from reference [1]. Copyright Elsevier 2022.

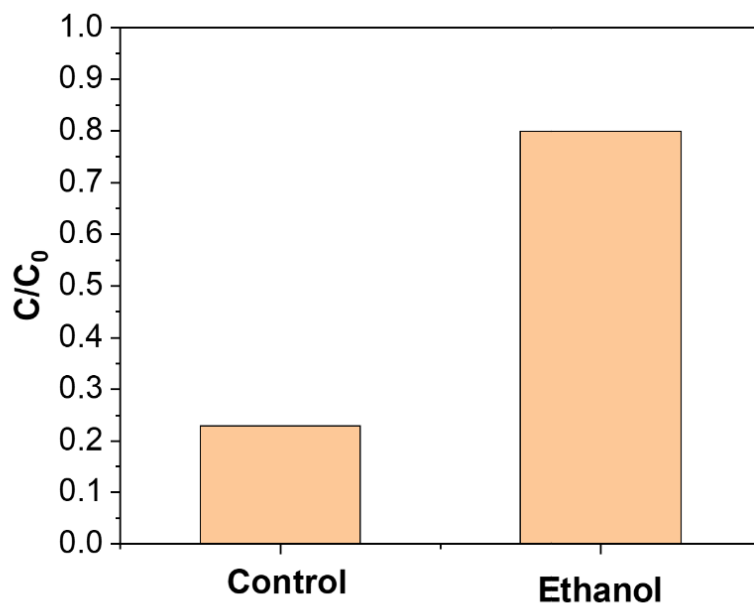


Figure B3.6 MB degradation in presence of ethanol as hole scavenger. Reproduced from reference [1]. Copyright Elsevier 2022.

B3. References

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Appendix C - Supplementary Information for Chapter 4

Table C4.1 Global atomic percentage deduced using XPS spectra of Ti_3AlC_2 and E- Ti_3AlC_2

Elements	Ti_3AlC_2	E- Ti_3AlC_2
C 1s (at. %)	27.4	20.70
Ti 2p (at. %)	15.4	21.40
Al 2p (at. %)	11.50	1.21
O 1s (at. %)	44.00	55.22

Table C.4.2 Performance of state-of-the-art photocatalysts at room temperature

Catalyst	Light Wavelength (nm)	Catalyst amount (mg)	Relative Humidity (%)	Inlet NO (ppm)	Reaction time (min)	NO conversion (%)	Selectivity (%)	DeNO _x	Ref.
B-TiO ₂	365	80	40	0.35	20	51	78	-	[1]
FeTi ₄	315-1050	0.55	50	0.1	60	~23	63	-	[2]
2CdTe/P25	315-400	200	50	1	~70	~35	~90	~0.3	[3]
25Ca/Ti	315-400	900	50	1	60	46	77	0.14	[4]
70Al/Ti	315-400	900	50	1	60	42	67	0	[4]
50 Ca/35Al/15 Ti	315-400	900	50	1	60	40	89	0.27	[4]
mpg-CN500	400-700	200	50	1	60	40	83	0.20	[5]
TiO ₂ -rGO-2	< 400	-	50	1	~30	52	-	-	[6]
TiO ₂ -HZSM-5(500)	365	20	50	1	30	25	-	-	[7]
BiOI	>400	-	50	1	30	5	83	-	[8]
9GQDs/CN	>380	80	50	20	60	90	74	0.19	[9]
Cubic-ZnSn(OH) ₆	250-900	200	70	0.5	30	75	-	0.27	[10]
TiO ₂ -g-C ₃ N ₄ -10	<400	-	50	1	30	30	-	0.18	[11]
Bi ₄ O ₅ Br ₂ /Bi ₂ S ₃ -60	420-780	150	50	0.5	15	60	90	-	[12]
PC105-TiO ₂	<400	800	40	1	~120	~50	40	-	[13]
TiO₂-Ti₃C₂-OH	320	130	50	1	120	54	91	0.30	This study

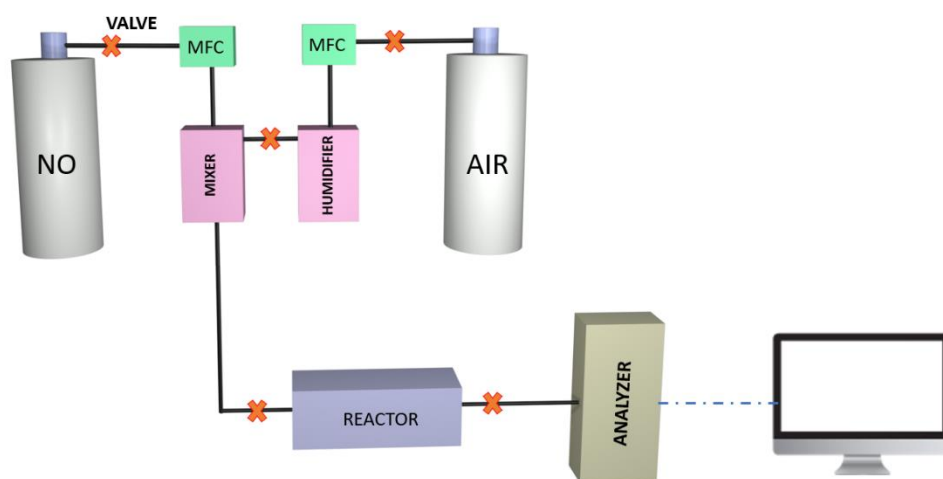


Figure C4.1 Schematic illustration of the reactor configuration constructed according to ISO standards. Reproduced from reference [14]. Copyright Elsevier 2022.

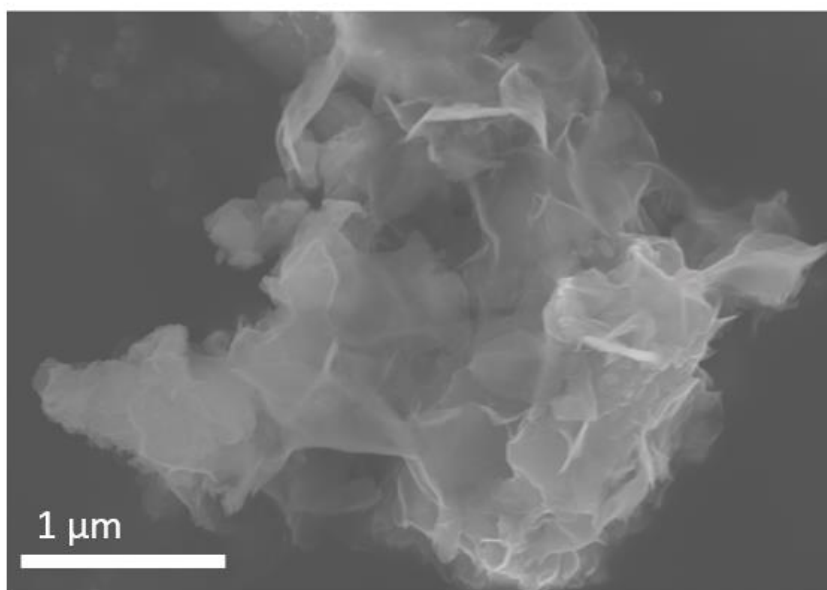


Figure C4.2 SEM image of E-Ti₃AlC₂. Reproduced from reference [14]. Copyright Elsevier 2022.

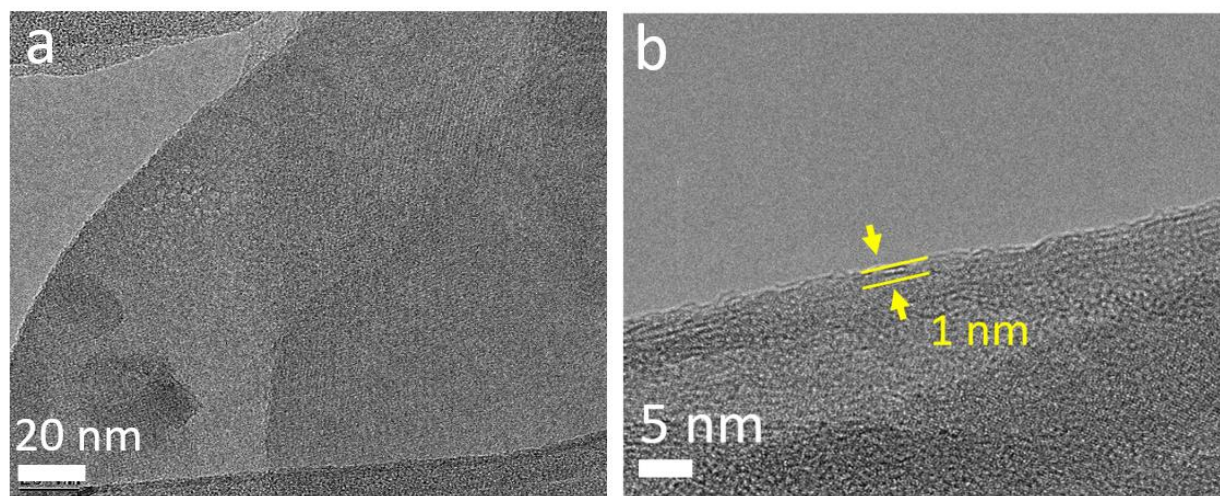


Figure C4.3 TEM images of $\text{Ti}_3\text{C}_2\text{-OH}$ show a one-layer $\text{Ti}_3\text{C}_2\text{-OH}$ sheet: a high-magnification image (a) and a high-resolution image (b). Reproduced from reference [14]. Copyright Elsevier 2022.

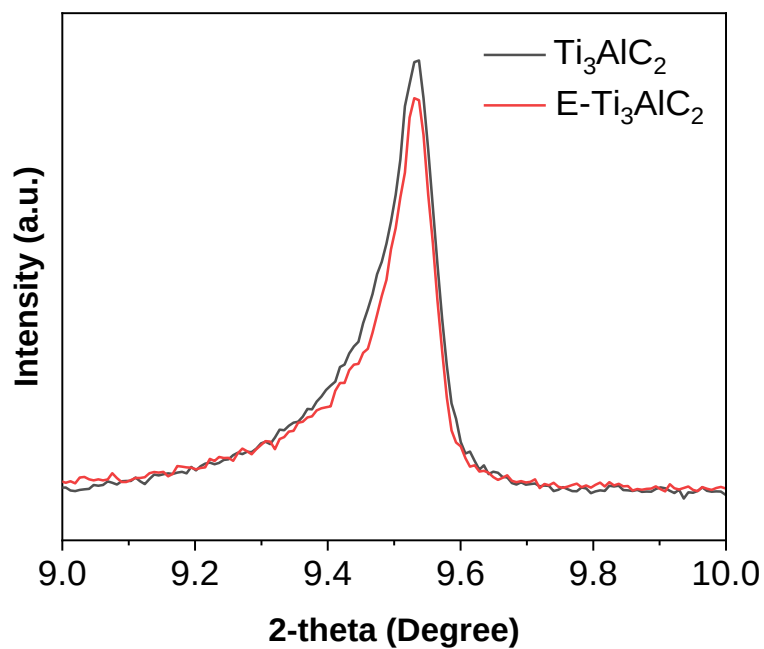


Figure C4.4 Zoom-in XRD patterns of Ti_3AlC_2 and $\text{E-Ti}_3\text{AlC}_2$ demonstrate the decrease in the intensity of the (002) peak after Al etching via NaOH. Reproduced from reference [14]. Copyright Elsevier 2022.

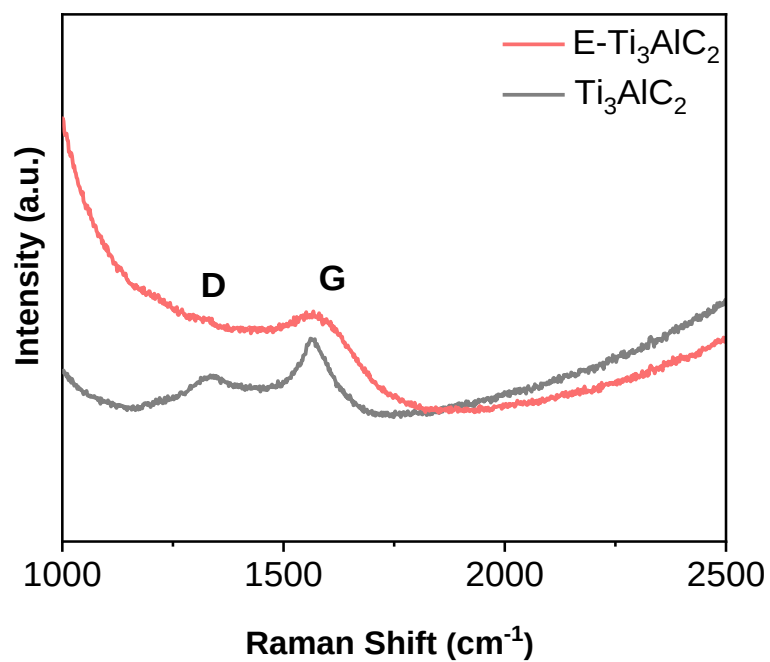


Figure C4.5 Raman spectra of Ti₃AlC₂ and E-Ti₃AlC₂ show the broadening in D- and G-band after Al etching with NaOH. Reproduced from reference [14]. Copyright Elsevier 2022.

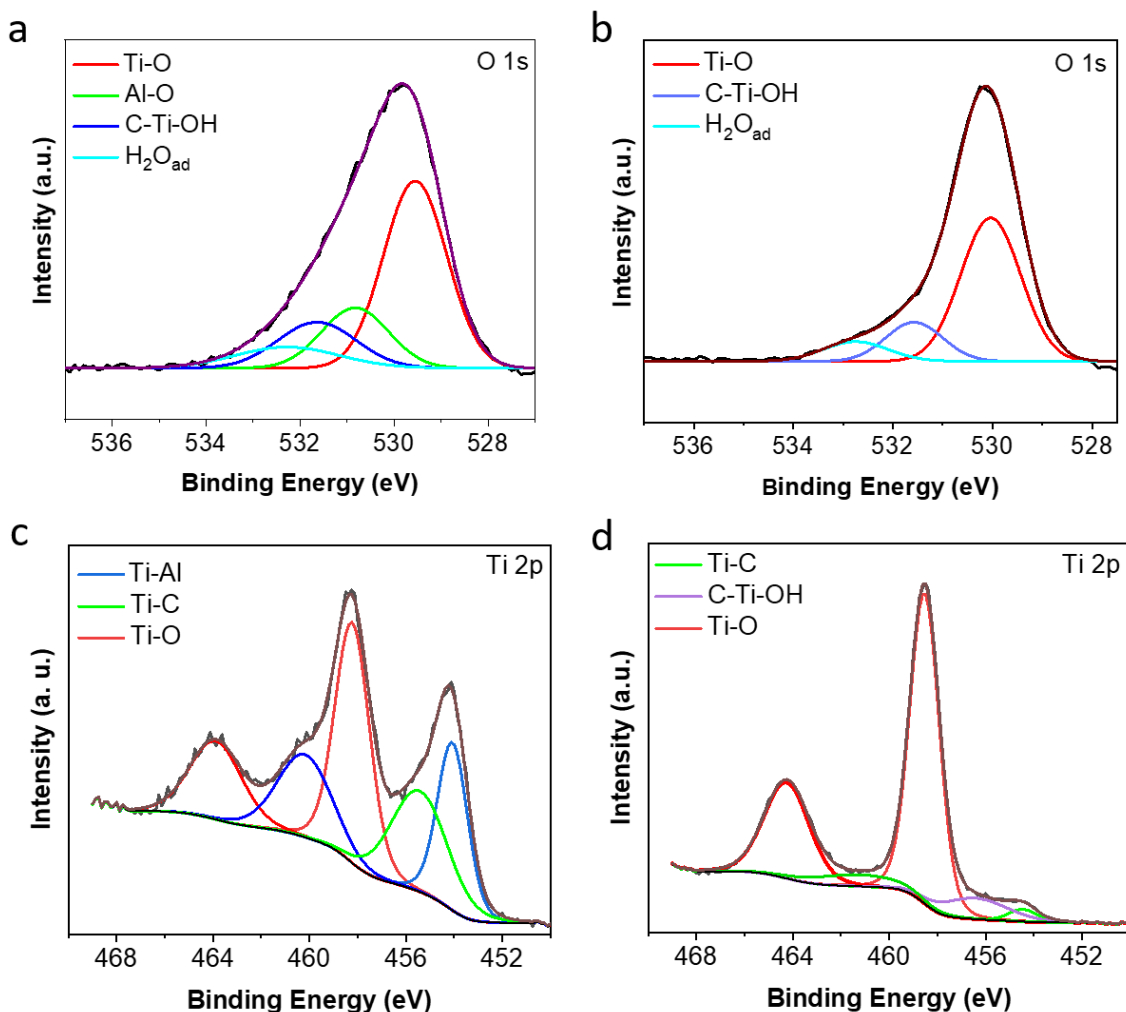


Figure C4.6 High-resolution XPS scans in O 1s region of Ti_3AlC_2 (a) and E- Ti_3AlC_2 (b). Peaks are assigned according to previous studies [15-18]. High-resolution XPS scans in Ti 2p region of Ti_3AlC_2 (c) and E- Ti_3AlC_2 (d). Peaks are assigned according to previous studies [16, 19-22]. Reproduced from reference [14]. Copyright Elsevier 2022.

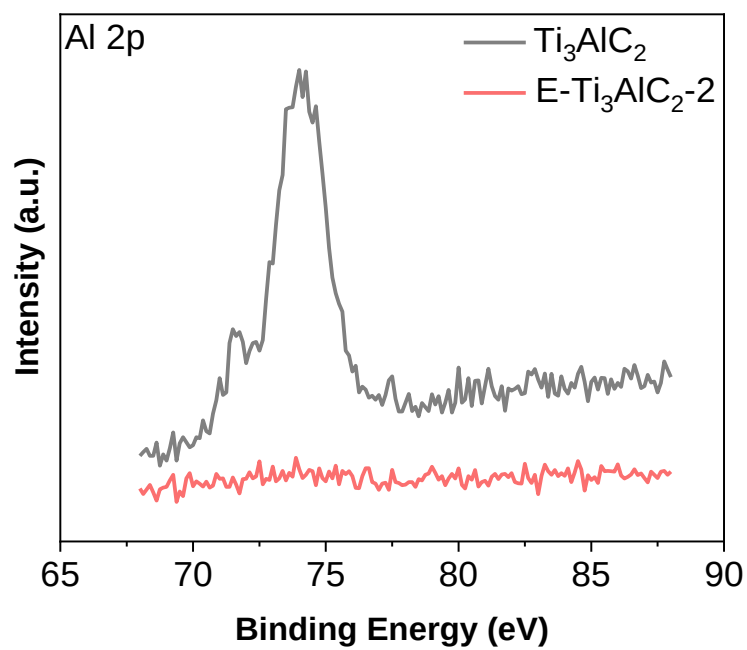


Figure C4.7 High-resolution XPS scans in Al 2p region of Ti_3AlC_2 and $\text{E-Ti}_3\text{AlC}_2\text{-2}$ show Al removal after NaOH treatment. Reproduced from reference [14]. Copyright Elsevier 2022.

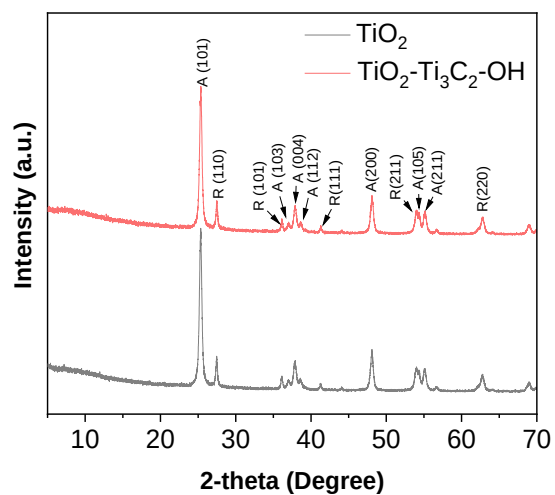


Figure C4.8 XRD patterns of TiO₂ and TiO₂-Ti₃C₂-OH. Reproduced from reference [14]. Copyright Elsevier 2022.

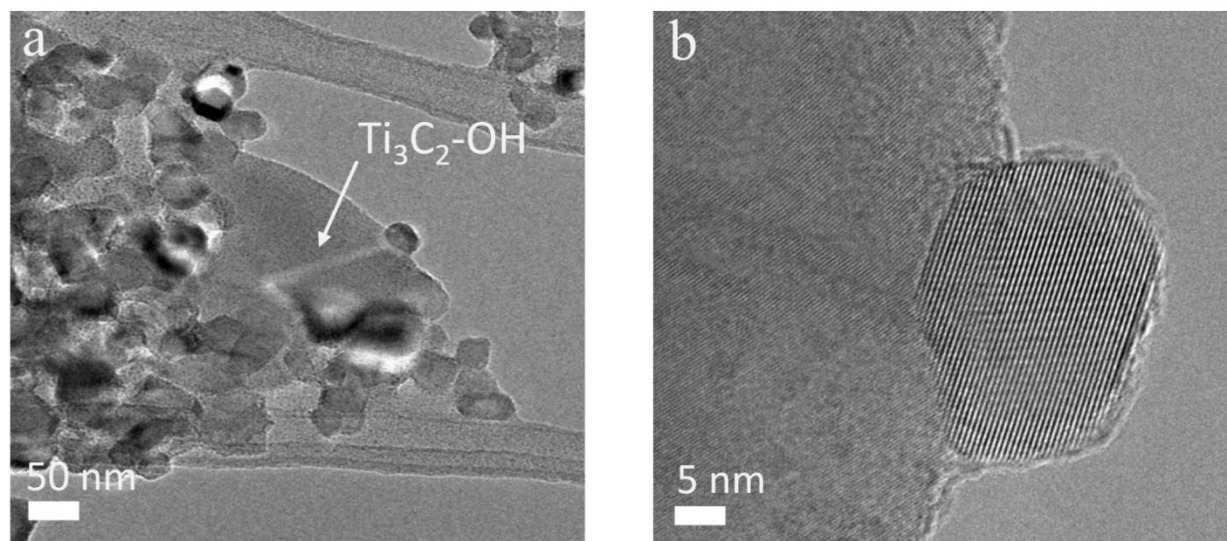


Figure C4.9 TEM image (a) and high-resolution TEM image (b) of $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$. Reproduced from reference [14]. Copyright Elsevier 2022.

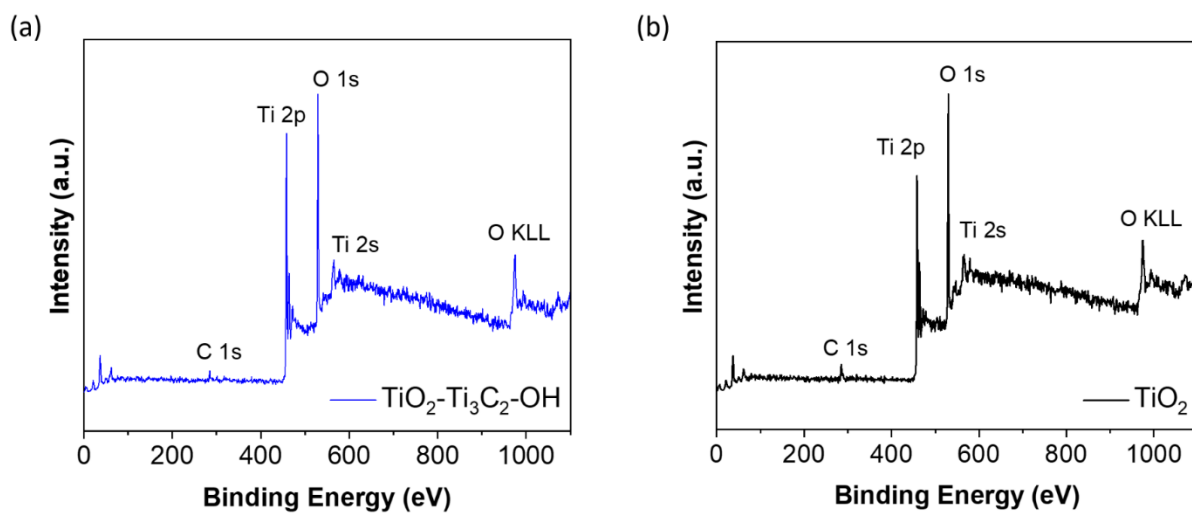


Figure C4.10 XPS survey scans of $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ (a) and TiO_2 (b). Reproduced from reference [14]. Copyright Elsevier 2022.

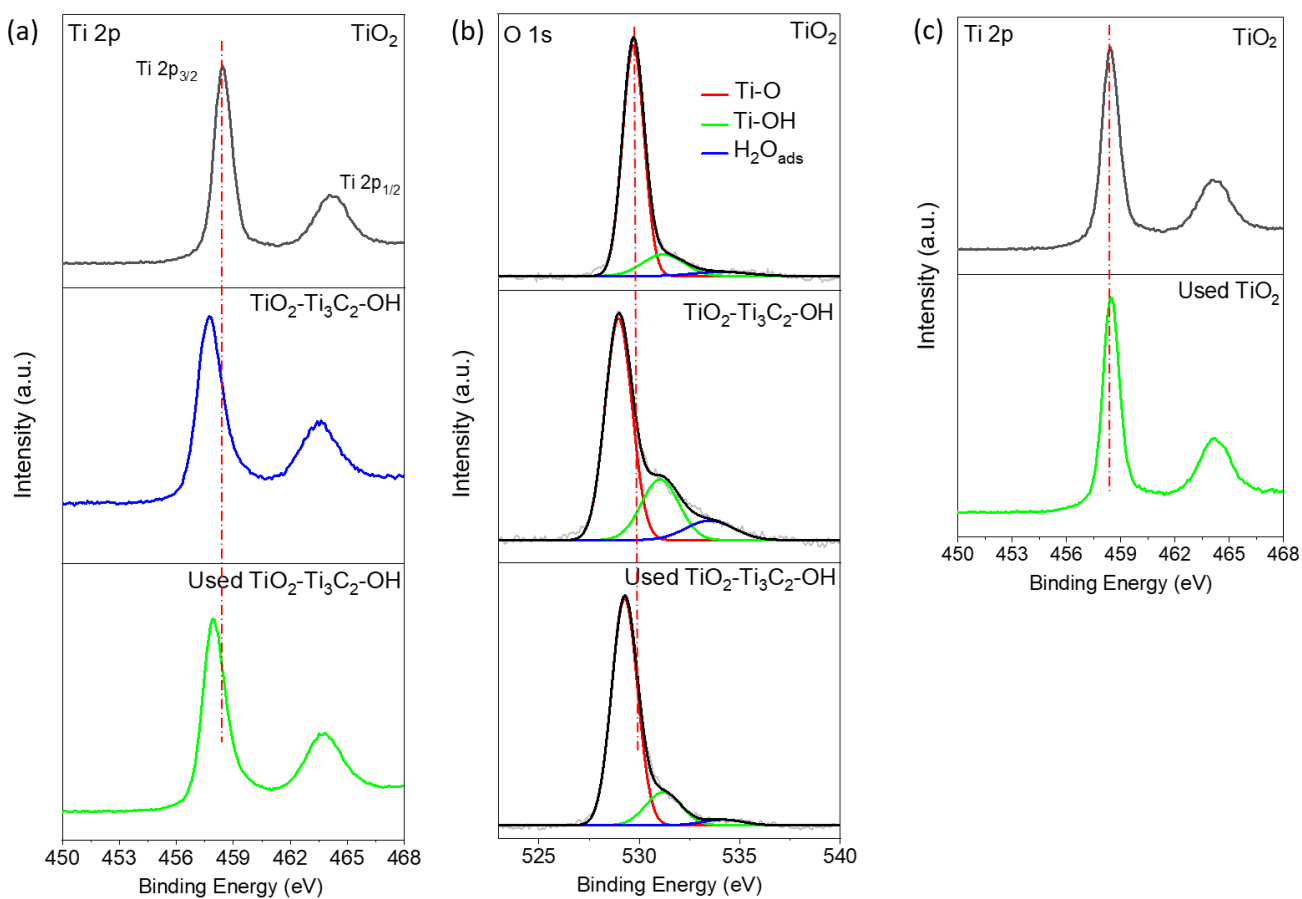


Figure C4.11 High-resolution XPS scans in Ti 2p and O 1s regions of TiO_2 and $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$. Used TiO_2 and $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ are the photocatalysts that have been used in photocatalytic oxidation of NO_x for 120 minutes. Reproduced from reference [14]. Copyright Elsevier 2022.

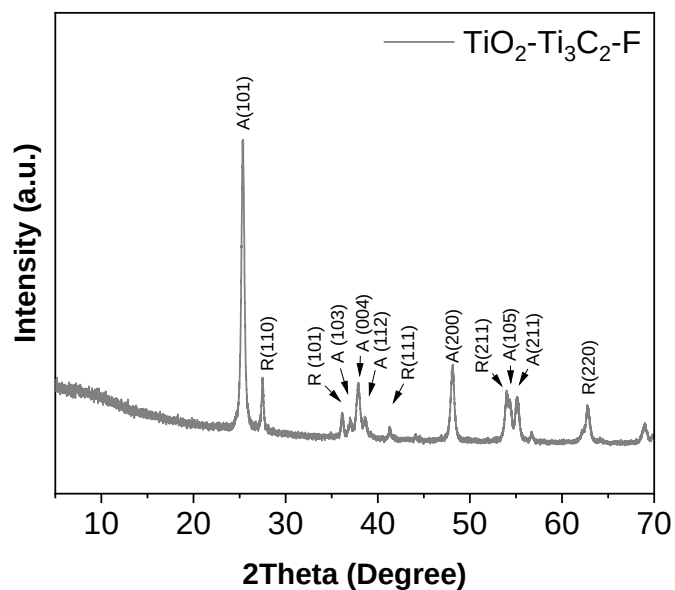


Figure C4.12 XRD pattern of $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-F}$. The diffraction peaks are indexed to several crystal planes of anatase TiO_2 (JCPDS No. 21-1272) and facets of rutile TiO_2 (JCPDS No. 21-1276) [23]. Reproduced from reference [14]. Copyright Elsevier 2022.

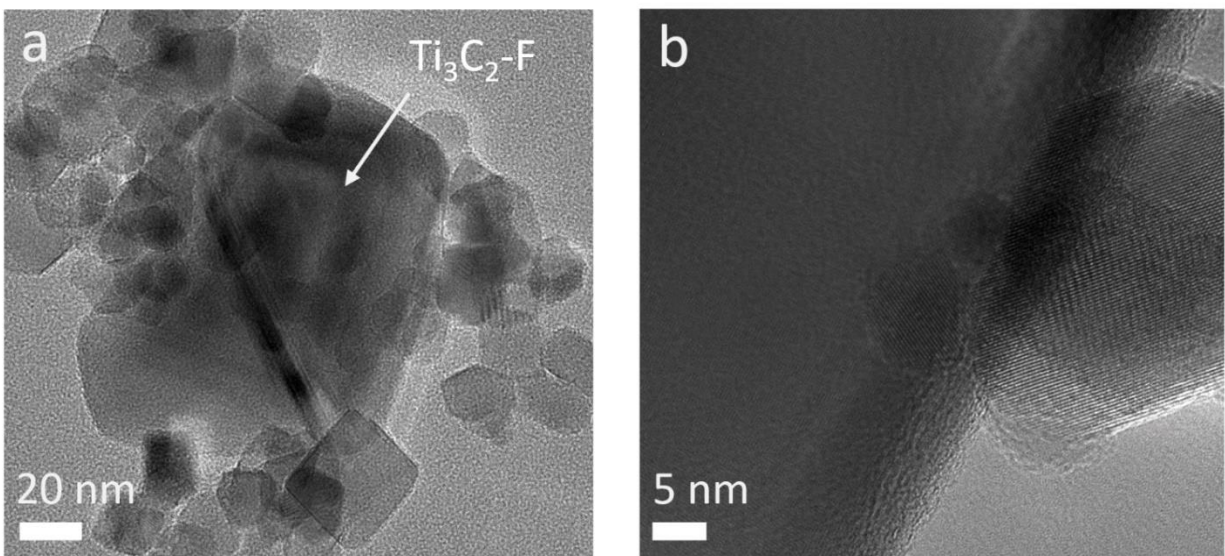


Figure C4.13 TEM image (a) and high-resolution TEM image (b) of $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-F}$. The high-resolution TEM image of $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-F}$ shows the intimate interaction between TiO_2 and $\text{Ti}_3\text{C}_2\text{-F}$. Reproduced from reference [14]. Copyright Elsevier 2022.

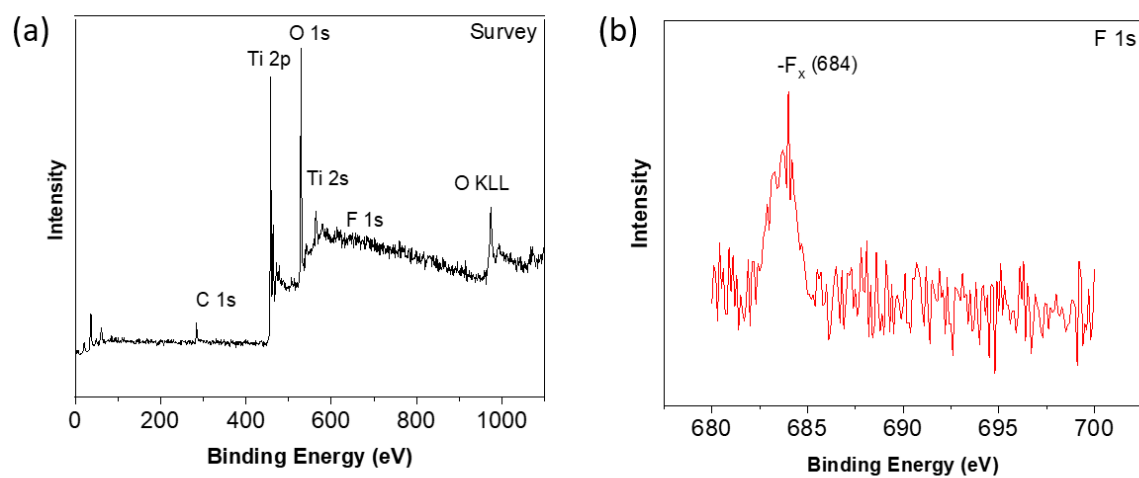


Figure C4.14 XPS survey scan of $TiO_2-Ti_3C_2-F$ (a) and high-resolution XPS scan in F 1s region of $TiO_2-Ti_3C_2-F$ (b). The high-resolution XPS spectrum in the F 1s region confirms the presence of $-F$ groups on $TiO_2-Ti_3C_2-F$ surface. Reproduced from reference [14]. Copyright Elsevier 2022.

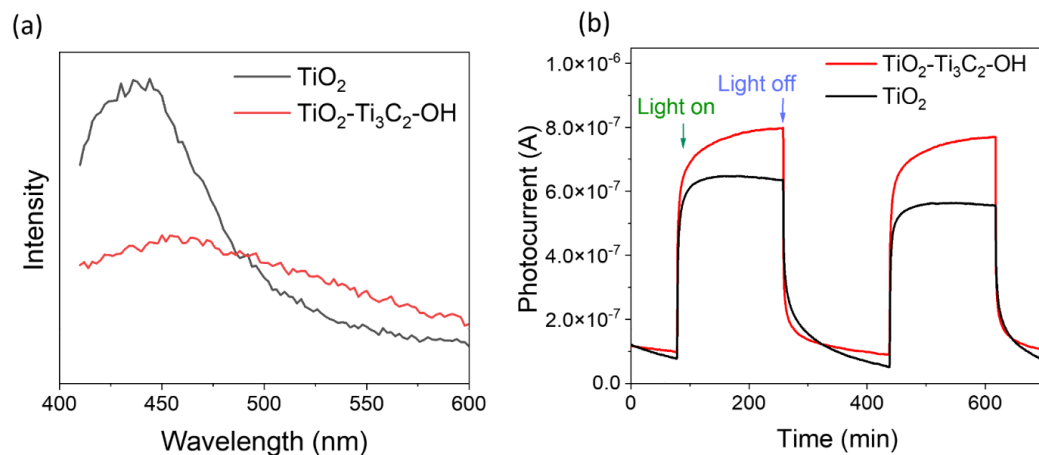


Figure C4.15 (a) Steady state PL spectra of TiO_2 and $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$. The quenching in PL intensity of TiO_2 after coupling with $\text{Ti}_3\text{C}_2\text{-OH}$, indicates the reduction in electron-hole recombination. (b) Transient photocurrent responses of TiO_2 and $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$. $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$ showed higher photocurrent compared with TiO_2 , confirming the effective electron-hole separation in $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-OH}$. Reproduced from reference [14]. Copyright Elsevier 2022.

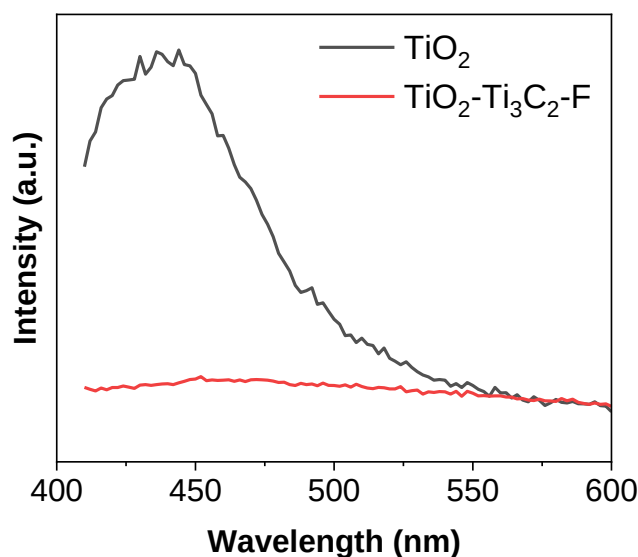


Figure C4.16. Steady state PL spectra of TiO_2 and $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-F}$. The quenching in PL intensity of TiO_2 after coupling with $\text{Ti}_3\text{C}_2\text{-F}$ indicates the reduction in electron-hole recombination. Reproduced from reference [14]. Copyright Elsevier 2022.

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Appendix D - Supplementary Information for Chapter 5

Table D5.1 TGA-deduced materials composition of TiO₂, g-C₃N₄, and TiO₂-g-C₃N₄.

Photocatalyst	TiO ₂ (wt%)	g-C ₃ N ₄ (wt%)
TiO ₂	100	-
g-C ₃ N ₄	-	100
TiO ₂ -g-C ₃ N ₄	20.5	79.5

Table D5.2 Global atomic percentage deduced using XPS spectra of TiO₂, g-C₃N₄, and TiO₂-g-C₃N₄.

Elements	TiO ₂	g-C ₃ N ₄	TiO ₂ -g-C ₃ N ₄
C (at.%)	21.9	47.7	43.5
Ti (at.%)	26.0	-	0.9
N (at.%)	0.9	49.0	52.0
O (at.%)	51.2	3.3	3.6

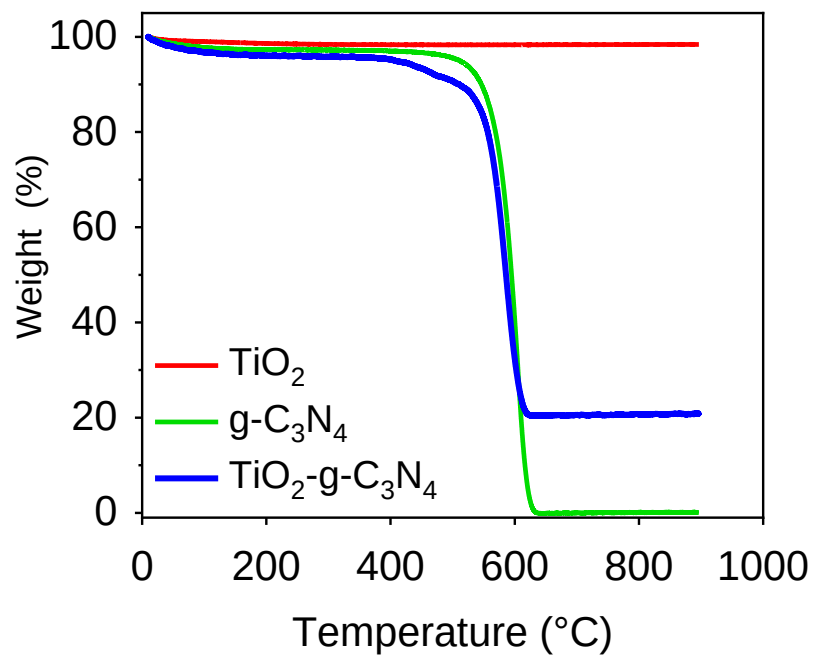


Figure D5.1 TGA profiles of TiO_2 , $\text{g-C}_3\text{N}_4$, and $\text{TiO}_2\text{-g-C}_3\text{N}_4$.

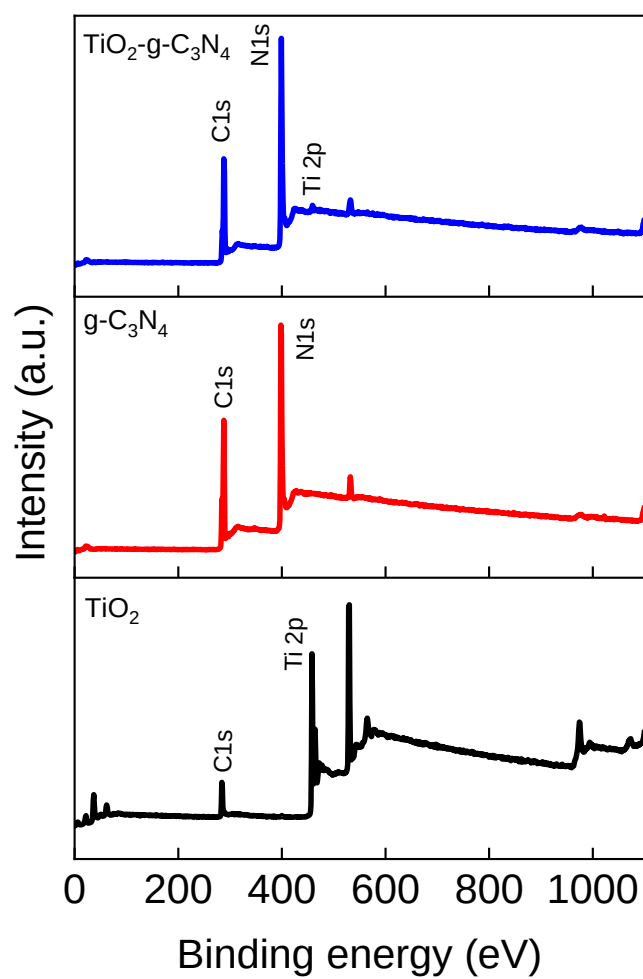


Figure D5.2 XPS survey spectra of TiO_2 , $\text{g-C}_3\text{N}_4$, and $\text{TiO}_2\text{-g-C}_3\text{N}_4$.

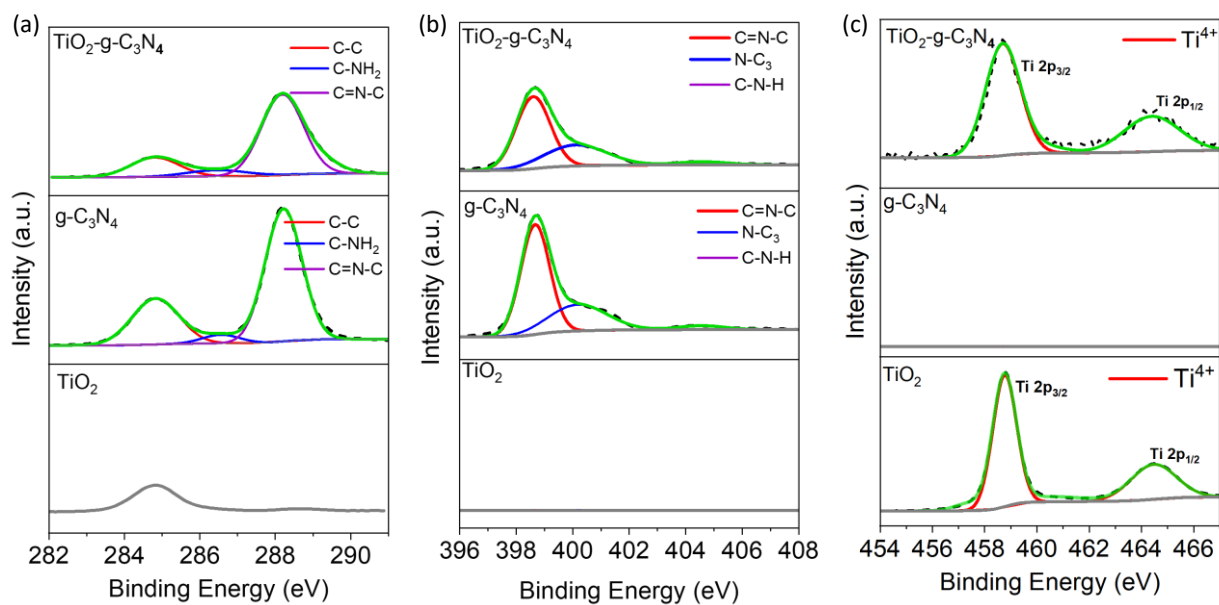


Figure D5.3 High-resolution XPS spectra in C1s (a), N1s (b), and Ti 2p (c) regions of TiO_2 , $\text{g-C}_3\text{N}_4$, and $\text{TiO}_2\text{-g-C}_3\text{N}_4$.

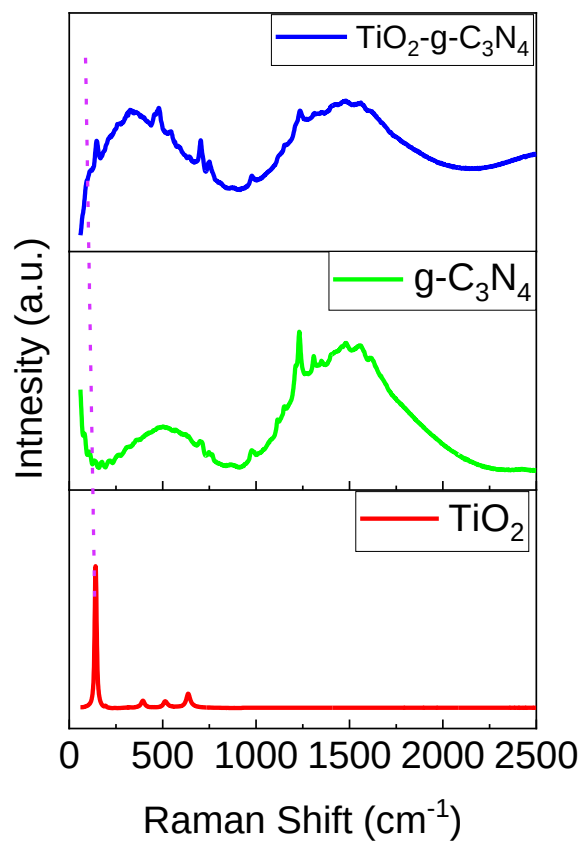


Figure D5.4 Raman spectra of TiO_2 , $\text{g-C}_3\text{N}_4$, and $\text{TiO}_2\text{-g-C}_3\text{N}_4$.

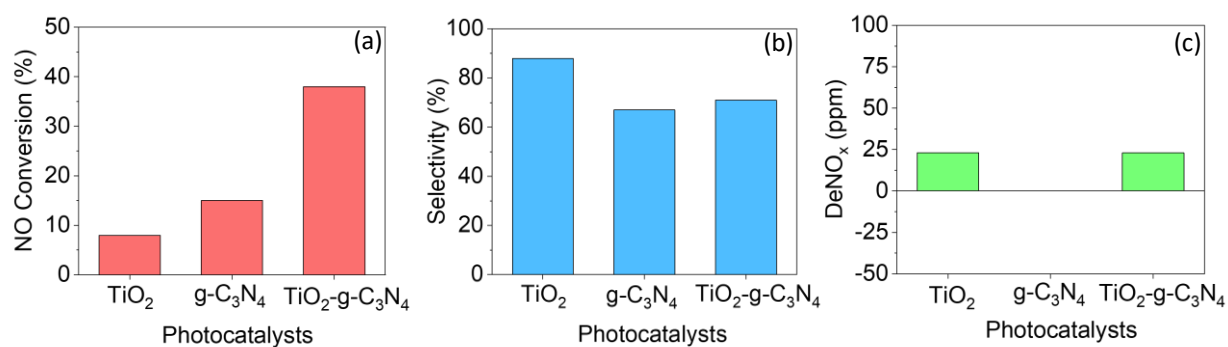


Figure D5.5 NO conversion(a), NO_x storage selectivity(b) and DeNO_x index (c) of TiO_2 , $\text{g-C}_3\text{N}_4$, and $\text{TiO}_2\text{-g-C}_3\text{N}_4$ under high humidity (50 %) and blue light.

Appendix E - Supplementary Information for Chapter 6

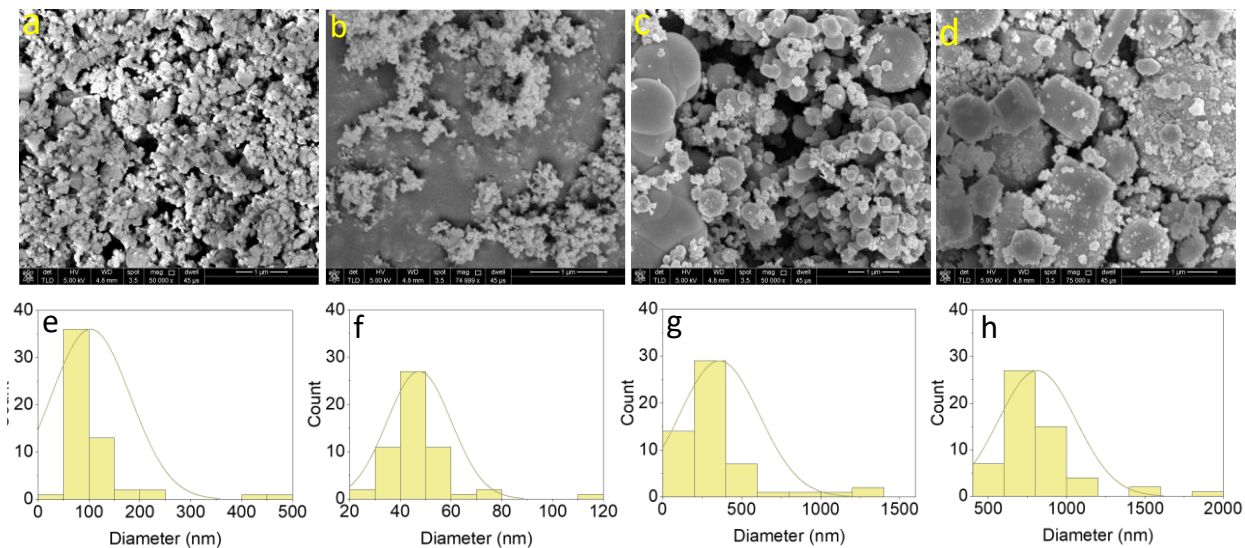


Figure E6.1 SEM image of detonation samples: (a) TiO₂-TiC-0.16, (b) TiO₂-TiC-0.38, (c) TiO₂-TiC-0.73, and (d) TiO₂-TiC-1. Size distribution histograms of detonation samples: (e) TiO₂-TiC-0.16, (f) TiO₂-TiC-0.38, (g) TiO₂-TiC-0.73, and (h) TiO₂-TiC-1.

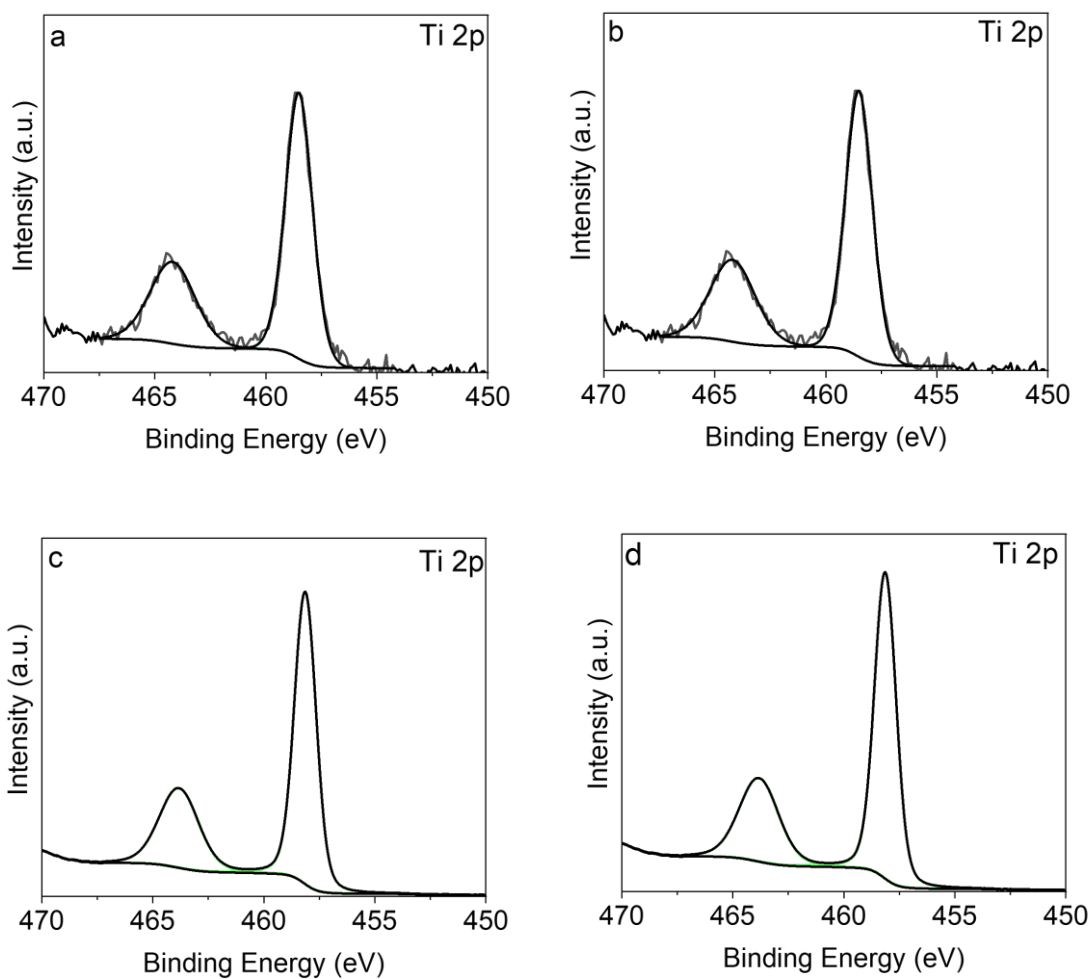


Figure E6.2 XPS analysis of detonation samples: (a) TiO₂-TiC-0.16, (b) TiO₂-TiC-0.38, (c) TiO₂-TiC-0.73, and (d) TiO₂-TiC-1.

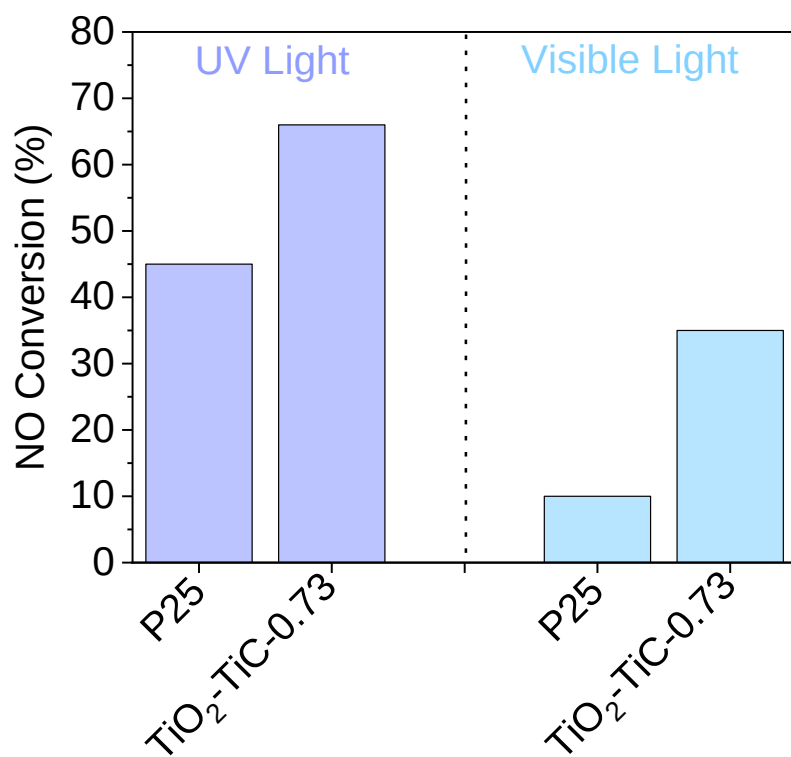


Figure E6.3 NO conversion of P25 and TiO₂-TiC-0.73 under UV and visible light.