Facile synthesis of C, N-TiO$_2$ nanorods via layered Ti$_3$O$_7^{2-}$-TMAH interlaminar bonding interaction and their enhanced catalytic performance

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Abstract

A green and efficient photocatalyst based on C and N co-doped titanium based nanorods (NRs) was prepared by facile hydrothermal synthesis and interlaminar bonding interaction between layered Ti$_3$O$_7^{2-}$ and tetramethylammonium hydroxide (TMAH). TMAH as one of quaternary ammonium-based compounds was used as the doping source of C and N elements. The results showed that C and N co-doping did not affect the anatase crystal structure of TiO$_2$ NRs. C, N-TiO$_2$ NRs showed excellent photocatalytic activity for degrading methyl orange under simulated sunlight irradiation. In particular, the 20:1 TiO$_2$ NRs catalyst showed the best catalytic performance, showing efficient photocatalytic rate of 90%. The photocatalytic reaction kinetics of undoped and doped catalysts was also studied. In addition, reactive species (RSs) experiments showed that hydroxyl radical (OH$^\cdot$), superoxide radical anions (O$_2^-\cdot$) and photogenerated holes (h$^+\cdot$) were major active species during the photocatalytic process. The mechanisms of the electrostatic attraction and potential photocatalytic degradation were proposed and discussed.

1. Introduction

More than 10 000 kinds of dyes per year, and moreover, the demand for printing and dyeing products has increased substantially in recent years [1–3]. However, the entry of dye wastewater into rivers and the food chain can have harmful effects on human health [4].

Photocatalysis has been widely employed as a green, non-secondary wastewater agent especially for dyeing wastewater treatment [5–9]. Photocatalytic nanomaterials have excellent degradation performance due to their high specific surface area [10–12]. In particular, TiO$_2$ nanomaterials appear to be a promising green catalyst due to its environmental safety, low cost and no secondary pollution [13–16]. However, low visible light utilization, the rapid recombination of electron-hole pairs and few surface reactive sites have obviously limited their practical applications [17].

In this respect, some non-metallic organic compounds (e.g. urea [18–20] and polyaniline [21]), noble metals [22, 23] and semiconductor composite [24] can be used to modify the surface of TiO$_2$ nanoparticles to enhance their photocatalytic activities, thereby effectively inhibiting the recombination of photoinduced carriers and broadening the absorption wavelength. Bonding interaction is an effective strategy for modifying catalyst materials. For instance, Wang et al prepared a nitrogen-doped TiO$_2$/graphene nanohybrid through self-assembly
of pyrene modified H$_2$Ti$_3$O$_7$ nanosheets and graphene via the $\pi-\pi$ stacking interactions [25]. Ota et al. reported that ethylenediamine-modified H$_2$Ti$_3$O$_7$ nanotube exhibit bonding interactions between the amines and OH groups on the surface of H$_2$Ti$_3$O$_7$ [26]. Due to the electronegativity of ions, the ions were adsorbed into the interlayer structure of nanotubes, leading to an improved photocatalytic performance of TiO$_2$ catalysts. However, interlaminar bonding interactions between layered titanates and TMAH (C–N doping source) has not been previously reported.

In this study, using TMAH as doping sources for C–N non-metallic elements, titanium-based nanorods were prepared and exhibited efficient photocatalytic degradation of dyes under simulated sunlight. This work can provide useful information and promote further interest in the preparation of C/N doped TiO$_2$ nanomaterials for photocatalytic degradation visible light irradiation.

2. Experimental section

2.1. Materials
All chemicals reagents were of analytical grade. P25 TiO$_2$ (80% anatase and 20% rutile crystalline phases) was supplied by Evonik Degussa GmbH. Ultrapure water with a resistance of 18.25 MΩ was provided by a water system (Milli-Q). NaOH, HCl (36%–38%), methanol and absolute alcohol were purchased from Chengdu Kelong Chemical. 25% aqueous solution of TMAH and Na$_2$C$_2$O$_4$ were purchased from Sinopharm Chemical Reagent. K$_2$Cr$_2$O$_7$ was provided by Macklin Chemical Reagent. Benzoquinone was purchased from Shandong Xiya Reagent. Methyl orange (MO) was purchased from Chengdu Kelong Chemical.

2.2. Synthesis of H$_2$Ti$_3$O$_7$ template
The synthetic process of H$_2$Ti$_3$O$_7$ nanotubes (NTs) was given as follows [27]. 22 g of NaOH was dissolved into 55 ml of ultrapure water to obtain solution. 1 g of P25 TiO$_2$ NPs was added into the solution. Then, the slurry was stirred vigorously at room temperature for 3 h. The resulting slurry was poured into a reactor, in which, was heated at 150 °C for 36 h. Thereafter, the obtained precipitates were washed with anhydrous alcohol and ultrapure water. Subsequently, 0.1 M of hydrochloric acid was added to the above obtained product and then vigorously stirred for 4 h to exchange Na$^+$ ions into H$^+$. After the reaction, the titanate nanotubes were rinsed with ultrapure water to make neutral. Then, the precipitates were dried at 80 °C for 10 h. Finally, H$_2$Ti$_3$O$_7$ template was obtained, which was porphyrized by an agate mortar.

2.3. Synthesis of C, N-TiO$_2$ nanorods
C, N-TiO$_2$ nanorods were prepared via facile hydrothermal synthesis and interlaminar bonding interaction method by using TMAH as the C and N sources. Briefly, H$_2$Ti$_3$O$_7$ NTs and 25% TMAH aqueous solution were added into 100 ml ultrapure water (mol ratios of Ti and N element were kept at 20:0.5, 20:1, 20:5, 20:10 and 20:15, respectively). The mixture was stirred for 6 h. The precipitates were washed with ultrapure water, which were dried at 80 °C for 10 h and then calcined at 600 °C for 5 h. Finally, the required samples were synthesized.

2.4. Characterization
The as-synthesized powder was conducted by x-ray diffraction patterns (XRD, Rigaku D/Max2500PC) with Cu Kα radiation (40 kV, 250 mA, $\lambda = 1.5418$). The XRD patterns were collected in the range 5° to 80°. The as-synthesized doped TiO$_2$ nanorods were performed on a scanning electron microscope (SEM, FEI Nova Nano SEM450) and transmission electron microscope (TEM, Thermo Fisher, Talos F200X). The diffuse reflectance spectroscopy and absorption spectra were measured with a UV–vis spectrophotometer (Shimadzu, UV-2550). X-ray photoelectron spectroscopy was measured with Al-Kα radiation (XPS, Thermo, EscaLab 250XI).

2.5. Photocatalytic reactions
25 mg of catalyst was dispersed in 50 ml MO aqueous solution (15 mg l$^{-1}$). After an adsorption–desorption equilibrium for 30 min, the MO aqueous solution was irradiated under simulated sunlight. During the photocatalytic process, samples were taken at intervals. The slurry was put into the centrifugal tube 4 ml at a rate of 12,000 rpm min$^{-1}$ for 3 min to remove the particles. The maximum absorbance of the sample was measured by UV–vis spectrophotometer. Finally, the percentage removal efficiency (%) were calculated as the following equations.

$$\text{Removal efficiency} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100$$

where $C_0$ and $C_e$ (mg l$^{-1}$) are the initial concentrations and concentrations after a period of time, respectively.
3. Results and discussion

3.1. Characterization of catalysts

XRD analysis was performed to study the crystal phase of the synthesized C, N-TiO₂ nanorods, as shown in figure 1. The diffraction peaks were shown as a tetragonal anatase phase [JCPDS No. 21-1272]. The peaks at 25.18°, 37.80°, 48.05°, 53.89°, 55.06°, 62.69°, 68.76°, 70.31° and 75.04° were assigned to the (101), (004), (200), (105), (211), (204), (116), (220) and (215) lattice planes of the anatase phase of TiO₂. This phenomenon demonstrated that the N doping process did not change the crystal structure of anatase phase, which indicated considerable stability of the TiO₂ sample. It is noteworthy that the (101) lattice plane gradually shifted to the high angle region with the increase of N content (figure 1(b)). Numerous studies showed that the doping of nitrogen would cause the shift of the diffraction peak of TiO₂ [28, 29]. Therefore, the reason is that N doping can cause lattice distortion, which lead to changes in the lattice parameters of TiO₂. Moreover, the 20:1 TiO₂ NRs showed a better crystallinity than that of 20:5 and 20:15 TiO₂ NRs. The reason was that a large amount of TMAH in the precursors can retard the formation of Ti-O-Ti network and decrease the crystallinity of TiO₂.

Figure 2 showed an SEM image of the agglomerated TiO₂ nanorods. The TiO₂ nanorods had an excellent one-dimensional rod-like shape. As observed, the diameter and length of TiO₂ nanorods were observed in the range of 15–20 nm and 50–200 nm, respectively. The length of the nanorods varied greatly due to the fracture of the nanorods during the calcination process. The EDS of 20:1 TiO₂ NRs shown in figure 3 showed the presence of Ti, O, C, and N elements. The presence of Pt was attributed to the sample holder of the EDS.

In order to further study the changes of chemical bonds in modified catalysts, the elemental composition and superficial chemistry of C, N-TiO₂ NRs were characterized by x-ray photoelectron spectroscopy (XPS). As indicated in figure 4(a), the C 1s consisted of four characteristic peaks. And the binding energies at 284.6, 285.2, 286.0 and 288.4 eV were vested in C–C, C–N, C–OH and C=O bonds, respectively, indicating that the catalyst contained C and N elements [30]. As shown in figure 4(b), the N 1s spectrum included two secondary peaks,

Figure 1. XRD patterns of TiO₂ nanorods and C, N co-doping TiO₂ nanorods in the 2θ range of (a) 5°–80° and (b) 23°–27°.

Figure 2. SEM images of 20:1 TiO₂ NRs. (a) Low- magnification and (b) high- micrographs.
which were located at 399.6 and 400.5 eV, corresponding to the N–Ti–O and N–C, respectively. The characteristic peak at 402.36 eV was related to the fragments of C and N molecules, which might be the residual organic molecule fragments of quaternary ammonium \[10, 29, 30\]. Moreover, in figure 4(c), the O 1s displayed three peaks at 529.5, 529.9 and 530.8 eV corresponding to Ti\textsuperscript{4+}–O, Ti–OH and N–Ti–O bonds, respectively. It showed that N element was doped into the TiO\textsubscript{2} lattice in the form of replacing oxygen atom. Ti-OH bonds on the surface of TiO\textsubscript{2} promoted the formation of ·OH during photocatalytic reaction \[29, 30\]. The Ti 2p spectrum (figure 4(d)) was split into four peaks at 458.2, 458.6, 463.7 and 464.4 eV which belonged to Ti\textsuperscript{3+}2p\textsubscript{3/2}, Ti\textsuperscript{4+}2p\textsubscript{3/2}, Ti\textsuperscript{3+}2p\textsubscript{1/2} and Ti\textsuperscript{4+}2p\textsubscript{1/2} bonds, respectively \[10, 29, 30\]. In addition, the atomic percentage of the catalyst elements obtained by XPS is shown in table 1.
3.2. Synthesis of co-doped NRs via interlaminar bonding interaction

TEM was used to characterize the morphology and microstructure of \( \text{H}_2\text{Ti}_3\text{O}_7 \) NTs (figures 5 and 6). As shown in figure 5(a), typical nanotubes of \( \text{H}_2\text{Ti}_3\text{O}_7 \) from several tens to hundreds of nanometers were observed in the as-prepared \( \text{H}_2\text{Ti}_3\text{O}_7 \) sample. Structures of 3–5 layers were also observed on the tube wall with the thickness of each layer of \( \sim 0.8 \) nm, as shown in figure 5(b). The outer diameter ranged in 5–15 nm and inner diameters in

![Figure 5](image)

**Figure 5.** (a) Typical TEM image of the as-prepared \( \text{H}_2\text{Ti}_3\text{O}_7 \) nanotubes, (b) Measurement of interlamellar spacing in the TEM image.

![Figure 6](image)

**Figure 6.** Layered walls structure and inner diameters of \( \text{H}_2\text{Ti}_3\text{O}_7 \) NTs in the TEM image.

| Catalysts        | C (at%) | O (at%) | Ti (at%) | N (at%) | Ti/O molar ratio | N/C molar ratio |
|------------------|---------|---------|----------|---------|------------------|-----------------|
| TiO\(_2\) NRs    | 67.66   | 32.34   |          |         | 1:2.09           | —               |
| 20:0.5 TiO\(_2\) NRs | 2.74    | 63.93   | 31.48    | 1.85    | 1:2.03           | 1:1.48          |
| 20:1 TiO\(_2\) NRs | 2.54    | 64.04   | 30.96    | 2.46    | 1:2.07           | 1:1.03          |
| 20:5 TiO\(_2\) NRs | 8.24    | 60.26   | 28.78    | 2.72    | 1:2.09           | 1:3.03          |
| 20:10 TiO\(_2\) NRs | 11.95   | 57.71   | 26.93    | 3.41    | 1:2.14           | 1:3.50          |

**Table 1.** Atomic percentage of elements of the C, N-TiO\(_2\) NRs catalysts.

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3–10 nm (figure 6). The above results revealed that the layered structure provided a large specific surface area, which can offer adsorption sites in the intermediate layer, thereby improving the photocatalytic efficiency.

Figure 7 illustrated the interionic adsorption process between tetramethylammonium cations and layered H$_2$Ti$_3$O$_7$ nanotubes. In the synthesis process, tetramethylammonium cations were attracted by layered H$_2$Ti$_3$O$_7$ nanotubes with a negative charge through electrostatic interaction. The interlayer spacing was 0.7–0.8 nm, which was in agreement with previous report [27]. The tube wall consisted of 3–5 layered structures. The surface negative charge was provided by -TiO$_3^2-$ between the nanotube wall layers. The layered Ti$_3$O$_7^{2–}$ structures offered adsorption sites to the TMAH cation. Tetramethylammonium cations of ~0.3 nm size can enter the space between the two layers. Therefore, the N and C elements from tetramethylammonium cations were distributed uniformly in the layered H$_2$Ti$_3$O$_7$ nanotubes.

3.3. Photocatalytic activity

Figure 8 showed the UV–vis diffuse-reflectance spectra of the catalysts. Pure TiO$_2$ NRs only showed light absorption within the UV region at an absorption edge of 388 nm. As expected, the C, N-TiO$_2$ showed an enhanced visible light absorption, that the absorption edge showed a slight red shift to 411 nm, as shown in figure 8. This indicated that the band gap was narrowed by the non-metal element doping. Based on the above results, the estimated bandgaps of pure TiO$_2$ NRs and C, N-TiO$_2$ NRs were 3.20 eV and 3.02 eV, respectively.
The TMAH doped photocatalyst possessed the narrow bandgap, perhaps due to interlaminar bonding interaction between layered Ti$_3$O$_7^{2-}$ and TMAH. It can enhance sunlight utilization and photocatalytic efficiency. In the presence of a 20:1 TiO$_2$ NRs catalyst in an aqueous solution at pH 7.0, the photocatalytic of MO was studied by UV-visible absorption spectra, as shown in figure 9(a). In the UV–vis spectra, obvious absorption peak change was observed at 464 nm. The degradation rate of MO in the presence of TiO$_2$ NRs and C, N-TiO$_2$ NRs are given in figure 9(b). Compared with pure TiO$_2$ NRs, C, N-TiO$_2$ NRs showed a slight adsorption of methyl orange. Under simulated sunlight irradiation for 150 min, 20:1 TiO$_2$ nanorods showed the highest photocatalytic activity, reaching 90% degradation efficiency.

The results indicated that small amount of C-N co-doping accelerated the photocatalytic oxidation reaction. Doping of non-metallic elements can change the valence band level and improve visible light response, which was consistent with the obtained XPS spectrum [31, 32]. Doping a certain amount of C or N into the TiO$_2$ lattice, the sample showed better photocatalytic activity. It can be observed in the O1s spectrum that as the doping amount increased, the N–Ti–O content also increased. However, the photocatalytic activity of the catalyst of 20:0.5 was the weakest compared with the catalysts of other ratios. Because the doping amount of the N element in the 20:0.5 catalyst was too low, the effect of the doping element was reduced. Moreover, when the doping amount of C and N exceeded the substitution ability of O in TiO$_2$, redundant non-metallic atoms would remain on the surface of the doped TiO$_2$ nanorods. The C1s energy spectrum proved that no C-Ti bond was formed, but carbon layers covering the surface of the catalyst was generated. In this case, much active sites of photocatalyst would be shielded by excess C/N atoms, so that the photocatalytic activity was suppressed.

In order to better compare the photocatalytic rate of the above catalysts, reaction kinetics of degradation of MO were showed in figure 9(c). The fitting curves were obtained from the reaction of pseudo first order model, that the kinetic expression was $-\ln(C/C_0) = kt$ [33, 34]. As can be seen, the 20:1 TiO$_2$ NRs catalyst presented the highest apparent rate constant ($k = 1.46 \times 10^{-2}$ min$^{-1}$), which was almost 7.9 and 8.3 times higher than those.

**Figure 9.** (a) UV–vis spectra of degrading MO in the presence of 20:1 TiO$_2$ NRs catalyst. (b) The degradation rate of MO in the presence of TiO$_2$ NRs and C, N-TiO$_2$ NRs under simulated sunlight. (c) Kinetic plots of MO in the presence of TiO$_2$ NRs and C, N-TiO$_2$ NRs. (d) Plots of photocatalytic active species trapped during photodegradation of MO by C, N-TiO$_2$ NRs (20:1) under simulated sunlight.
of the doped TiO$_2$ nanorods and undoped TiO$_2$ nanorods, respectively. Table S1 listed the comparison of the catalytic rate of C, N-TiO$_2$ NRs with other catalysts. Non-metallic of C and N elements doping can introduce impurity levels around at O$_{2p}$ band level. It can inhibit the recombination of photon-generated carriers, which can effectively increase the electrons and holes used in the radical reaction $^{[30, 35–37]}$. However, excessive N element doping would inhibit the catalytic rate, as shown in figure S2.

During the photocatalytic degradation of organic pollutants, various reactive species (RSs) have different functions when C, N-TiO$_2$ was used as catalyst. Methanol (1:15/V:V), benzoquinone (50 μM), Na$_2$C$_2$O$_4$ (10 mM), and K$_2$Cr$_2$O$_7$ (2 mM) were used to scavenge ·OH, ·O$_2^-$, $h^+$ and e$^-$, respectively $^{[33, 38]}$. It should be pointed out through the addition performed discrepant inhibitory effects on the photocatalytic degradation of MO (figure 9(d)). When no scavenger was added, 15 mg l$^{-1}$ MO can be degraded within 150 min and the photocatalytic efficiency reached 90%. When K$_2$Cr$_2$O$_7$ was added, the photodegradation efficiency decreased slightly, which indicated that e$^-$ was not the main active species. Nevertheless, methanol, Na$_2$C$_2$O$_4$ and benzoquinone recorded obvious inhibitory effects during the degradation of MO with inhibition rate of 75.3%, 79.7% and 95.5%, respectively. In the catalytic reaction, the undoped TiO$_2$ showed the same active radical, as shown in figure S3. No other reactive groups were produced. Therefore, these results demonstrated that ·OH, $h^+$ and ·O$_2^-$ were the major reactive species toward the degradation of MO, while e$^-$ showed a minor effect.

Based on the above dates, the potential photodegradable mechanisms were demonstrated in scheme 1. Under simulated sunlight, the valence band (VB) electrons of C, N-TiO$_2$ NRs were excited to the conduction band (CB), leading to the generation of $h^+$ and e$^-$. According to the relatively strong electron affinity of N atoms in free tetramethylammonium cations, electrons in the CB can be easily transferred to tetramethylammonium cations, so that inhibited the recombination of e$^-$/h$^+$ pairs. Subsequently, the e$^-$ contacted with H$_2$O or O$_2$ in solution, accompanied by a series of free radical chain reaction, leading to the generation of ·O$_2^-$, that a fraction of ·O$_2^-$ reacted with H$^+$ to generate ·OH. Moreover, a portion of $h^+$ reacted with H$_2$O molecule, resulting in the generation of ·OH. Consequently, the production of RSs (·OH, ·O$_2^-$ and $h^+$) would attack MO, leading to its efficient photodegradation. Thus, C, N-TiO$_2$ NRs showed excellent photocatalytic degradation performance.

4. Conclusion

In summary, novel carbon-nitrogen co-doped titanium based nanorods were prepared by facile hydrothermal synthesis and interlaminar bonding interaction. Tetramethylammonium cations were electrostatically attracted by layered H$_2$Ti$_3$O$_7$ nanotubes with a negative surface charge. Tetramethylammonium cations entered into the space between two layers of nanotubes. Therefore, N and C elements from tetramethylammonium cations were distributed uniformly in layered H$_2$Ti$_3$O$_7$ nanotubes. The as-synthesized C, N-TiO$_2$ nanorods had a length of 50–200 nm and a diameter of 15–20 nm. From the elemental analysis of the SEM microdomain, it was concluded that the catalyst contained C and N elements. Moreover, the C, N-TiO$_2$ nanorods exhibited better photocatalytic properties for degrading MO under simulated sunlight irradiation. The 20:1 TiO$_2$ NRs catalyst presented the highest apparent rate constant, which was almost 8.3 times higher than that of undoped TiO$_2$.
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References

[1] Fleischmann C, Lievenbruck M and Ritter H 2015 Polymers and dyes: developments and applications Polymers 7 717–46
[2] Grace Pavithra K, Senthil Kumar P, Jaikumar V and Sundar Rajan P 2019 Removal of colorants from wastewater: a review on sources and treatment strategies J. Ind. Eng. Chem. 75 1–19
[3] Virekant K, Giri B S, Raza N, Roy K, Kim K H, Rai B N and Singh R S 2018 Recent advancements in bioremediation of dye: current status and challenges Bioresource Technol. 283 355–67
[4] Rasheed T, Bilal M, Nabeel F, Adeel M and Iqbal H M N 2019 Environmentally-related contaminants of high concern: potential sources and analytical modalities for detection, quantification, and treatment Environ. Int. 122 52–66
[5] Liang S, Zhang D, Pu X, Yao X, Han R, Yin J and Ren X 2019 A novel Ag3O2/g-C3N4 p–n heterojunction photocatalysts with enhanced visible and near-infrared light activity Sep. Purif. Technol. 210 786–97
[6] Wang Y, Wang X, Zhang M, Fang L, Lin L, Gao J, Zhang Y, Yang B, He G and Sun Z 2019 TiO2 nanorod array film decorated with rGO nanosheets for enhancing photocatalytic and photoelectrochemical properties J. Alloy. Compd. 770 243–51
[7] Cerron-Calle O A, Aranda-Aguirre A J, Luysy C, Garcia-Segura S and Alarcon H 2019 Photoelectrochemical decolorization of azo dyes with nano-composite oxide layers of ZnO nanorods decorated with Ag nanoparticles Chemosphere 219 296–304
[8] Wang X, Wang L, Guo D, Ma L-L, Zhu B-L, Wang P, Wang G-C, Zhou S-M and Huang W-P 2019 Fabrication and photocatalytic performance of C, N, F-tridoped TiO2 nanotubes Catal. Today 327 182–9
[9] Chen Y, Zhang Y, Luo L, Shi Y, Wang S, Li L, Long Y and Jiang F 2018 A novel templated synthesis of C/N-doped β-Bi2O3 nanosheets for synergistic rapid removal of 17a-ethynylestradiol by adsorption and photocatalytic degradation Ceram. Int. 44 2178–85
[10] Sanchez-Martinez A, Ceballos-Sanchez O, Koop-Santa C, Lopez-Mena E R, Orozco-Guareño E and García-Guadarrama M 2018 N-doped TiO2 nanoparticles obtained by a facile coprecipitation method at low temperature Ceram. Int. 44 5273–83
[11] Rajini C, Dhallak D, Kim T H, Yamaguchi T and Lee S W 2018 Fabrication of Ag-decorated BiOBr-mBiVO4 dual heterojunction composite with enhanced visible photocatalytic performance for degradation of malachite green Nanotechnology 29 154001
[12] Mohammad Alasfur F K, Ridha N J, Jumali M H H and Radiman S 2018 One-step formation of TiO2 hollow spheres via a facile microwave-assisted process for photocatalytic activity Nanotechnology 29 145707
[13] Yang J, Zhang X, Liu H, Wang C, Liu S, P, Wang L and Liu Y 2013 Heterstructured TiO2–WO3 porous microspheres: preparation, characterization and photocatalytic properties Catal. Today 201 195–202
[14] Khan M M, Adil S F and Al-Mayouf A 2015 Metal oxides as photocatalysts J. Saudi. Chem. Soc. 19 462–4
[15] Arekhi M and Jamshidi M 2018 Influences of inorganic binder on photocatalytic oxidation (PCO) and degradation of nano/micro TiO2-containing acrylic composites Prog. Org. Coat. 115 1–8
[16] Seo J, Lee H, Lee H-J, Kim M S, Hong S W, Lee J, Cho K, Choi H and Lee C 2018 Visible light-photosensitized oxidation of organic pollutants using amorphous perosso-titania Appl. Catal. B: Environ. 225 487–95
[17] Linsebigler A L, Lu G and Yates J T 1995 Photocatalysis on TiO2 surfaces: principles, mechanisms, and selected results Chem. Rev. 95 735–58
[18] Zhou S, Liu Y, Li J, Wang Y, Jiang G, Zhao Z, Wang D, Duan A, Liu J and Wei Y 2014 Facile in situ synthesis of graphitic carbon nitride (g-C3N4):N–TiO2 heterojunction as an efficient photocatalyst for the selective photoreduction of CO2 to CO Appl. Catal. B: Environ. 158–159 20–9
[19] Makropoulu T, Panagiotopoulou P and Venieri D 2018 N-doped TiO2: photocatalysts for bacterial inactivation in water J. Chem. Technol. Biotechn. 93 2518–26
[20] Mohamed M A, Zain M M F, Jeffery Minggu L, Kassim M B, Jaafar J, Saidina Amin N A and Ng Y H 2019 Revealing the role of kapok as bio-template for In-situ construction of C-doped g-C3N4@C, N co-doped TiO2 core–shell heterojunction photocatalyst and its photocatalytic hydrogen production performance Appl. Surf. Sci. 476 205–20
[21] Hung C H, Yuan C and Li H W 2017 Photodegradation of diethyl phthalate with PANI/CNT/TiO2 immobilized on glass plate irradiated with visible light and sunlight-effect of synthesized method and pH J. Hazard. Mater. 322 243–53
[22] Somalingam K, McDonagh A, Zhou J L, Johir M A H and Ahmed M B 2018 Photocatalysis of estrone in water and wastewater: comparison between Au–TiO2 nanocomposite and TiO2, and degradation by-products Sci. Total Environ. 610–611 521–30
[23] Liu W, Wei C, Wang G, Cao X, Tan Y and Hu S 2019 In situ synthesis of plasmonic Ag@AgI/TiO2 nanocomposites with enhanced visible photocatalytic performance Ceram. Int. 45 17884–9
[24] Zhang R, Wang Q, Zhang J, Lu Q, Liu W, Yin S and Cao W 2019 Towards efficient photocatalytic degradation of organic pollutants in hierarchical TiO2/SnO2-p-n heterojunction under visible-light irradiation Nanotechnology 30 434001

nanorods. Reactive species (RSs) scavenging experiments revealed that -OH, h+ and -O2 — were the major reaction species in the degradation of MO. Hence, our results demonstrated that interlaminar bonding interaction was a promising technology for the facile synthesis of non-metal doped titanium-based nanomaterials.
[25] Wang R, Wu Q, Lu Y, Liu H, Xia Y, Liu J, Yang D, Huo Z and Yao X 2014 Preparation of nitrogen-doped TiO2/graphene nanohybrids and application as counter electrode for dye-sensitized solar cells ACS Appl. Mater. Inter. 6 2118–24
[26] Ota M, Hirota Y, Uchida Y, Sakamoto Y and Nishiyama N 2018 Low temperature synthesized H2Ti3O7 nanotubes with a high CO2 adsorption property by amine modification Langmuir 34 6814–9
[27] Song L, Zhao X, Cao L, Moon J W, Gu B and Wang W 2015 Synthesis of rare earth doped TiO2 nanorods as photocatalysts for lignin degradation Nanoscale 7 16695–703
[28] Chen Q et al 2019 N-doped TiO2 photocatalyst coatings synthesized by a cold atmospheric plasma Langmuir 35 7161–8
[29] Qin Y, Li H, Lu J, Meng F, Ma C, Yan Y and Meng M 2020 Nitrogen-doped hydrogenated TiO2 modified with G2S nanorods with enhanced optical absorption, charge separation and photocatalytic hydrogen evolution Chem. Eng. J. 384 123272
[30] Huang H, Song Y, Li N, Chen D, Xu Q, Li H, He J and Lu J 2019 One-step in situ preparation of N-doped TiO2@C derived from Ti3C2 MXene for enhanced visible-light driven photodegradation Appl. Catal. B: Environ. 251 154–61
[31] Senthilnathan J and Philip L 2010 Photocatalytic degradation of lindane under UV and visible light using N-doped TiO2 Chem. Eng. J. 161 83–92
[32] Guo S, Tang Y, Xie Y, Tian C, Feng Q, Zhou W and Jiang B 2017 P-doped tubular g-C3N4 with surface carbon defects: universal synthesis and enhanced visible-light photocatalytic hydrogen production Appl. Catal. B: Environ. 218 664–71
[33] Li Y, Xue Y, Tian J, Song X, Zhang X, Wang X and Cui H 2017 Silver oxide decorated graphitic carbon nitride for the realization of photocatalytic degradation over the full solar spectrum: from UV to NIR region Sol. Energy. Mat. Sol. C 168 100–11
[34] Hu X, Liu X, Tian J, Li Y and Cui H 2017 Towards full-spectrum (UV, visible, and near-infrared) photocatalysis: achieving an all-solid-state Z-scheme between Ag2O and TiO2 using reduced graphene oxide as the electron mediator Catal. Sci. Technol. 7 4193–205
[35] Zhang F, Zhang Y, Zhang G, Yang Z, Dionysiou D D and Zhu A 2018 Exceptional synergistic enhancement of the photocatalytic activity of SnS2 by coupling with polyaniline and N-doped reduced graphene oxide Appl. Catal. B: Environ. 236 53–63
[36] Liu C, Zhu H, Zhu Y, Dong P, Hou H, Xu Q, Chen X, Xi X and Hou W 2018 Ordered layered N-doped KTiNbO5/g-C3N4 heterojunction with enhanced visible light photocatalytic activity Appl. Catal. B: Environ. 228 54–63
[37] Wang F et al 2017 Facile synthesis of N-doped carbon dots/g-C3N4 photocatalyst with enhanced visible-light photocatalytic activity for the degradation of indomethacin Appl. Catal. B: Environ. 207 103–13
[38] Li G, Nie X, Chen J, Jiang Q, An T, Wong P K, Zhang H, Zhao H and Yamashita H 2015 Enhanced visible-light-driven photocatalytic inactivation of Escherichia coli using g-C3N4/TiO2 hybrid photocatalyst synthesized using a hydrothermal-calcination approach Water Res. 86 17–24