mpg-C₃N₄/anatase TiO₂ with reactive {001} facets composites to enhance the photocatalytic activity of organic dye degradation

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mpg-C₃N₄/anatase TiO₂ with reactive {001} facets composites were synthesized via a facile ultrasonic dispersion method. Incorporation of mpg-C₃N₄ into anatase TiO₂ was successfully confirmed by X-ray diffraction (XRD). The percentage of exposed {001} facets in TiO₂ calculated from the Raman spectra was 80.6%. The microstructure and optical properties of the as-prepared samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption–desorption isotherms, UV-vis diffuse reflectance spectra (DRS) and photoluminescence (PL) spectroscopy. The effects of mass ratios of mpg-C₃N₄/(TiO₂ + mpg-C₃N₄) on the photocatalytic activities of the mpg-C₃N₄/TiO₂ composites were investigated. The photocatalytic experiments indicated that the mpg-C₃N₄/TiO₂ composites showed a much higher photocatalytic activity than the pristine TiO₂ and mpg-C₃N₄ for the degradation of methylene blue (MB) under UV light and visible light irradiation. This enhancement should be attributed to the reactive {001} facets of TiO₂ and the heterojunction formed at the interface between anatase TiO₂ and mpg-C₃N₄, thus resulting in a much lower recombination rate of the photoinduced electrons and holes. Compared with the decolorization process, mineralization is slower. The degradation of 2,4-dichlorophenol suggests that the dye sensitization is not the main cause of dye degradation. In addition, the quenching effects of different scavengers proved that the superoxide radicals (·O₂⁻) and holes (h⁺) were the main factors for the improved photoactivity under UV-visible light, while the superoxide radicals (·O₂⁻) play important roles in the photocatalytic reaction under visible light irradiation. Repeatability experiments of MB degradation suggest that the mpg-C₃N₄/TiO₂ composites have high stability. The photocatalytic degradations of MB, RhB and MO were measured under UV and visible light irradiation and the photocatalytic degradation efficiency was found to be in the decreasing order of RhB > MB > MO. These results indicate that the incorporation of mpg-C₃N₄ into anatase TiO₂ with reactive {001} facets is an effective method to improve the photocatalytic activity under both UV and visible light.

1. Introduction

Semiconductor photocatalysts have attracted great interest due to their potential applications in treating environmental deterioration and utilizing solar energy.1–3 Among all semiconductors used as photocatalysts, titanium dioxide (TiO₂) has attracted much attention from numerous researchers due to its environmental friendliness, low cost and long-term stability against photo and chemical corrosion.4–6 For anatase TiO₂, both theoretical and experimental studies have found that the minority {001} facets in the equilibrium state are more reactive than the {101} facets.7,8 So, since Yang et al.⁹ reported well-defined, high-purity and uniform anatase TiO₂ single crystals with the exposure of a large percentage of reactive {001} facets, many efforts have been focused on developing new routes for preparing TiO₂ with dominant {001} facets.⁹–¹² However, it can only absorb UV light, which occupies less than 4% of the solar energy. In addition, the high recombination rate of photoinduced electron–hole pairs is another factor limiting its photocatalytic efficiency. Thus, various modification methods have been developed to overcome these problems, including metal doping,¹¹ nonmetal doping,¹⁴ surface modification,¹⁵ and heterojunction construction.¹⁶ Among these methods, constructing heterojunctions can significantly enhance photocatalytic activity due to the efficient charge separation and transportation between the interfaces of different semiconductors.

Graphitic carbon nitride (g-C₃N₄) with layered structure similar to graphene has been reported to be an excellent candidate for photocatalysis under visible light irradiation.
owing to its unique structure and electronic properties.\textsuperscript{17-18} g-
C\textsubscript{3}N\textsubscript{4} is a thermal, chemical, and photochemical stable semi-
conductor because of its tri-s-triazine (C\textsubscript{6}N\textsubscript{7})-based building
blocks, and strong covalent bonds between carbon and nitride atoms.\textsuperscript{19,20} And it has been prepared through various tech-
niques.\textsuperscript{21,22} Furthermore, the narrow bandgap energy of about
2.7 eV endows the polymeric semiconductor with visible-light
absorbing ability up to 460 nm, and the highest occupied
molecular orbital (HOMO) position of g-C\textsubscript{3}N\textsubscript{4} is 1.62 eV,\textsuperscript{23} which is
higher than valence bands (VB) of the most photocatalysts,
hence the holes on the VB of other components can easily
transfer to the HOMO of g-C\textsubscript{3}N\textsubscript{4}. However, the photocatalytic
performance of g-C\textsubscript{3}N\textsubscript{4} is still limited due to quick recombina-
tion of the carriers and a very small surface area which cannot
provide more possible reaction sites for the catalytic reaction.

Chen et al. has successfully prepared the ZnO@mpg-C\textsubscript{3}N\textsubscript{4} core-
shell structures\textsuperscript{24} and found that compared with g-C\textsubscript{3}N\textsubscript{4}, meso-
oporous g-C\textsubscript{3}N\textsubscript{4} (mpg-C\textsubscript{3}N\textsubscript{4}) can in principle enhance the light
harvesting ability and the reactant adsorption capability of the
material. In addition, it becomes easier to coat on the other
catalyst’s surface than g-C\textsubscript{3}N\textsubscript{4} due to many pores on the sheet of
mpg-C\textsubscript{3}N\textsubscript{4}.

In this article, a series of mpg-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} with reactive \{001\}
facets composites were successfully prepared by using a facile
ultrasonic dispersion method and then characterized by various
facets composites were systematically evaluated by decomposition of methane blue (MB) under both UV and visible light irradiation. In order to
prepare a new type photocatalyst with high photocatalytic
activity, the in

2.1. Chemicals and materials
All reagents used were of analytical purity and were used
without further purification. Titanium tetrafluoride (TiF\textsubscript{4}),
cyanamide, ammonium bifluoride (NH\textsubscript{4}HF\textsubscript{2}), and tert-butyl
alcohol (TBA) were obtained from Sinopharm Chemical
Reagent Beijing Co., Ltd. P25, methylene blue (MB), methyl
orange (MO), rhodamine B (RhB), 2,4-dichlorophenol, diso-
dium ethylenediaminetetraacetate (EDTA-2Na), hydrochloric
acid (HCl), sodium hydroxide (NaOH), methanol and ethanol
were purchased from Beijing Chemical Works. 40% dispersion
of SiO\textsubscript{2} particles (particle diameter 12 nm) was supplied by
Beijing BOYU GOKE New Material Technology Co., Ltd, PR
China.

2.2. Synthesis of as-synthesized samples
2.2.1. Synthesis of anatase TiO\textsubscript{2} microspheres with reactive
\{001\} facets. The formation of anatase TiO\textsubscript{2} microspheres is
based on hydrolysis of titanium tetrafluoride (TiF\textsubscript{4}) under the
hydrothermal conditions of high temperature and acid. In
a typical synthesis,\textsuperscript{19} 60 mL of 0.04 M TiF\textsubscript{4} aqueous solution,
which was prepared by adding 0.297 g of TiF\textsubscript{4} into 60 mL of 0.01
M HCl solution, was poured into 100 mL Teflon-lined stainless
autoclave and heated at 200 °C for 4 h. After synthesis, the
autoclave was cooled to room temperature naturally, and the
products were collected by centrifugation, washed with 0.01 M
NaOH aqueous solution and deionized water several times.
Finally the products were dried in the oven at 60 °C for 12 h.

2.2.2. Synthesis of mpg-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2}. The mpg-C\textsubscript{3}N\textsubscript{4} was prepared
with the hard template method according to the ref. 17 with
small modification. First, an amount of 3.0 g molten cyanamide
was heated and stirred at 70 °C, and the 40% dispersion of 12
nm SiO\textsubscript{2} particles (7.5 g) were added dropwise. The mixture was
heated at 90 °C with stirring to evaporate water. Then the
resultant transparent mixtures were heated at a rate of 2.3 °C
min\textsuperscript{-1} over 4 h to reach a temperature of 550 °C, and tempered
at this temperature for an additional 4 h. To remove the silica
templates, the obtained brown-yellow powders were treated
with ammonium bifluoride (NH\textsubscript{4}HF\textsubscript{2}, 4 M) for two days. The
powders were then centrifuged and washed with distilled water
for four times and with ethanol twice. Finally the mpg-C\textsubscript{3}N\textsubscript{4} was
dried at 70 °C under vacuum for several hours.

2.2.3. Synthesis of mpg-C\textsubscript{3}N\textsubscript{4}/anatase TiO\textsubscript{2} with reactive
\{001\} facets composites. The synthetic procedure of mpg-C\textsubscript{3}N\textsubscript{4}/
TiO\textsubscript{2} composites was depicted as follows. Firstly, a certain
amount of mpg-C\textsubscript{3}N\textsubscript{4} was added into 50 mL of methanol with
sonication for 30 min to completely disperse the mpg-C\textsubscript{3}N\textsubscript{4}.
Then, the anatase TiO\textsubscript{2} was added into the above suspension
liquid and magnetically stirred in a fume hood until all meth-
anol evaporated. Finally, an opaque powder was obtained after
drying at 100 °C. A series of mpg-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} composites with the
different mass ratios of mpg-C\textsubscript{3}N\textsubscript{4}/(TiO\textsubscript{2} + mpg-C\textsubscript{3}N\textsubscript{4})
were synthesized by this method, which denoted as mpg-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2}–
X (X = 1%, 2%, 3%, 4%, 5%, 6%, 7%, 10%, 20%).

2.3. Characterization of as-synthesized samples
X-ray diffraction (XRD) patterns of the powders were recorded at
room temperature by a D8 Advance X-ray diffractometer. Raman
spectra were recorded on an inVia Raman microscope (Renishaw)
at the range of 100–800 cm\textsuperscript{-1}. Morphologies and
structures of the as-prepared samples were further examined
with a HITACHI HT7700 transmission electron microscopy
(TEM) operated voltage of 100 kV. High-resolution transmission
electron microscopy (HRTEM) images were obtained by a JEOL
JEM-2010 field emission transmission electron microscope with
an accelerating voltage of 200 kV. TEM images were observed on a
Hitachi S4800 Field-Emission Scanning Electron Microscope
at an accelerating voltage of 15.0 kV. Nitrogen adsorption–
desorption isotherm was obtained at 77.35 K with an Autosorb-
IQ-2MP (Quanmetrics Instruments) automated gas sorption
analyzer. The pore size distribution was obtained from the BJH (Barrett–Joyner–Halenda)
method. The UV-vis diffuse reflectance spectra (DRS) of the
samples were recorded in the range from 200 to 850 nm using
2.4. Photocatalytic evaluation

The photocatalytic activities were evaluated by the degradation of MB, MO, RhB and 2,4-dichlorophenol under UV light and visible light irradiation in the photochemical reaction instrument (BL-GHX-IV). UV light was provided by a 500 W mercury lamp. Visible light was obtained from a 500 W xenon lamp. The as-prepared photocatalyst (25 mg for UV light, 50 mg for visible light) was totally dispersed in an aqueous solution of dyes (50 mM, 0.01 mM). Before the irradiation, the photocatalyst powder and dye solution were vigorously stirred in the dark for 2 h to ensure the establishment of an adsorption–desorption equilibrium. After that, the light was turned on, and temperature of the system was controlled by a water bath (22 ± 1 °C) running through the outer casing of the glass tube to avoid light induced heating. At certain time intervals, 5 mL aliquots were sampled and centrifuged to remove the particles. The concentration of the dye was analyzed by recording the variation of the absorption-band maximum in the visible spectrum of MB (664 nm), MO (464 nm), RhB (554 nm) and 2,4-dichlorophenol (284 nm) solution using a UV765 UV-vis spectrophotometer. Total organic carbon of the illuminated solution at different time intervals was measured by the TOC analyzer (Shimadzu, L-series).

Stability of the catalyst was tested by reusing the catalyst for repeated cycles of experiment after a photocatalytic reaction. After each cycling test, the sample was collected and washed with distilled water via centrifugation, then the as-obtained sample were dried at 80 °C for 8 h for next cycling reused.

2.5. Active species trapping experiments

To detect the active species generated during photocatalytic reaction, some sacrificial agents, such as tert-butyl alcohol (TBA, 1 mM), disodium ethylenediaminetetraacetate (EDTA-2Na, 1 mM) were used as the scavengers of hydroxyl radical (·OH) and hole (h+), respectively.25–27 And superoxide radical (·O2−) was excluded by bubbling N2 into system with a gas flow rate of 30 mL min−1 (101.3 kPa, 20 °C). This trapping experiment was similar to the above photodecomposition experiment except that the sacrificial agent was added, respectively.

3. Results and discussion

3.1. Characterization of as-synthesized samples

The phase structures of the as-synthesized photocatalysts were characterized by X-ray diffraction (XRD). The wide-spectra (20.0–70.0°) and narrow-spectra (26.0–29.0°) XRD patterns of TiO2, mpg-C3N4 and mpg-C3N4/TiO2 composites are shown in Fig. 1. All the diffraction peaks of as-synthesized TiO2 can be indexed to the anatase phase by careful comparison with JCPDS card file no. 21-1272, indicating its high purity. No spurious diffractions due to crystallographic impurities such as rutile or brookite were identified. The reflection peaks are considerably sharp, indicating that the sample is well crystallized. For mpg-C3N4, the main diffraction peak at 2θ = 27.2° represents the stacking of the conjugated aromatic system,28,29 like the case in graphite. Fig. 1 shows that the crystal phase of TiO2 does not change after having been composited with the mpg-C3N4 and its diffraction peaks are in good agreement with the anatase TiO2. However, no obvious diffraction peaks of mpg-C3N4 were observed in the mpg-C3N4/TiO2 composites. This phenomenon might be caused by the low mpg-C3N4 loading amount and the diffraction peak of TiO2 at 25.2° is too strong to show the peak of mpg-C3N4 at 27.2°. In order to clearly observe the peaks of mpg-C3N4 in mpg-C3N4/TiO2 composites, the narrow-spectra XRD patterns in the region of 2θ (26.0–29.0°) were tested. Compared with anatase TiO2, there is a weak diffraction peak at 27.2° in mpg-C3N4/TiO2 composites.

As shown in Fig. 2(a), the as-synthesized TiO2 microspheres have an average size of around 2.5 μm. The surface of the microsphere is a mosaic structure which covered with interconnected square nanoflakes. Fig. 2(c) shows transmission electron microscopy (TEM) images of TiO2, and Fig. 2(d) is the high resolution transmission electron microscopy (HRTEM) images of rectangular region in Fig. 2(c). The lattice fringes indicated that interplanar instance is 0.239 nm, which is in good agreement with the spacing of the corresponding (001) plane of the anatase TiO2, indicating that the flat regions on the external edge of the anatase TiO2 microspheres are the projection of the anatase {001} facets.3,30 Fig. 2(b) shows the TEM images of mpg-C3N4. The TEM pictures indicate that the pore size and connectivity of those powders exactly reflect the geometric properties of the original template. The disordered pore system of spherical pores with a mean diameter of 12 nm can be regarded as a negative image of the structure of the silica sol.17 Different from the anatase TiO2 with well-defined edges and corners, the mpg-C3N4/TiO2 composite displays an irregular edge (Fig. 2(e)). The interplanar instance of the outermost irregular edges is about 0.33 nm (Fig. 2(f)), corresponding to the spacing of {002} plane in g-C3N4 (d = 0.336 nm, JCPDS 87-1526).11 Through an ultrasonic dispersion method in CH3OH...
methanol, the mpg-C₃N₄ exfoliated into sheet structures and coated on the surface of anatase TiO₂ microspheres to achieve a minimum surface energy.

Raman spectroscopy was used to measure the percentage of exposed {001} facets in TiO₂. Fig. 3 shows that the peaks appeared at 144.1, 396.2, 514.1 and 630.1 cm⁻¹, which indicated the typical anatase TiO₂ phase and was also consistent with the XRD results. It has been known that the Eg peak is mainly caused by symmetric stretching vibration of O–Ti–O in TiO₂, the B₁g peak is caused by symmetric bending vibration of O–Ti–O, and the A₁g peak is caused by antisymmetric bending vibration of O–Ti–O. The higher the percentage of {001} facets are exposed, the less the number of the symmetric stretching vibration modes of O–Ti–O will be, and the more the number of the symmetric bending vibration and the antisymmetric bending vibration of O–Ti–O. Correspondingly, the intensity of the Eg peaks in the Raman spectra becomes decreased, and the intensity of the A₁g and B₁g peaks become increased.

Based on the ratio of the peak intensity of Eg at 144.1 cm⁻¹ and the peak intensity of A₁g at 514.1 cm⁻¹, the percentage of exposed {001} facets in TiO₂ was calculated to be 80.6% according to a new approach reported by Tian et al.³³

Fig. 4 shows the nitrogen adsorption–desorption isotherms (Fig. 4(a)) and corresponding curve of the pore size distribution (Fig. 4(b)) for anatase TiO₂, mpg-C₃N₄ and mpg-C₃N₄/TiO₂. The adsorption–desorption isotherms in Fig. 4(a) show that all the samples are of type IV (BDDT classification), suggesting the presence of mesopores (2–50 nm). The isotherm of TiO₂ is of type H3, indicating the presence of slit-shaped pores resulted from aggregation of plate-like particles. This result is in close agreement with the SEM observations of square nanoflakes (Fig. 2(a)). The isotherm of mpg-C₃N₄ is classified as type IV with a H1 hysteresis loop, indicating the existence of a narrow pore size distribution. The pore diameter of mpg-C₃N₄ is 12.401 nm, which is related to the 12 nm silica templates. It is well known that samples with enlarged surface areas readily exhibit enhanced photocatalytic capability, mainly owning to the abundant active sites exposed and large light harvesting. Compared to pure TiO₂, the isotherms and pore size distributions of the mpg-C₃N₄/TiO₂ shift up with the increase of mpg-C₃N₄, indicating the photocatalysts with higher surface areas and pore volumes after mixing with mpg-C₃N₄.

The UV-vis diffuse reflectance spectra of the anatase TiO₂, mpg-C₃N₄ and mpg-C₃N₄/TiO₂ are shown in Fig. 5. It can be seen a sharp basal absorption edge for anatase TiO₂ occurs at 391 nm, which agrees well with the band gap of TiO₂ (3.2 eV). The pure mpg-C₃N₄ exhibits the fundamental absorption edge at of 465 nm, corresponding to the band gap of 2.7 eV. The UV-vis DRS spectrum of mpg-C₃N₄/TiO₂ is quite similar to anatase TiO₂, but the main absorption edge moves toward the visible light region. In addition, with increasing the content of mpg-C₃N₄ in photocatalysts, there was a red shift of the UV-vis absorption edge for all mpg-C₃N₄/TiO₂ composites, indicating the decrease in the band gap. This is considered to be beneficial to produce the photogenerated electron–hole pairs under UV light irradiation and the visible light absorption was improved after mixing with mpg-C₃N₄.
3.2. Photocatalytic activity of as-synthesized samples

The photocatalytic activities of the mpg-C$_3$N$_4$/TiO$_2$ samples were evaluated by degradation of methylene blue (MB) in solution under the UV and visible light irradiation. As shown in Fig. 6(a), when the mass ratios of mpg-C$_3$N$_4$/TiO$_2$ are 1%, 2% and 3%, the composites exhibit a more efficient photodegradation rate than the pristine TiO$_2$ and mpg-C$_3$N$_4$ under UV light irradiation. The photocatalytic activity of mpg-C$_3$N$_4$/TiO$_2$ increases gradually with the increase of mass ratio of mpg-C$_3$N$_4$/TiO$_2$ and the mpg-C$_3$N$_4$/TiO$_2$–3% exhibits the most significantly enhanced photocatalytic performance. This change in UV activity of mpg-C$_3$N$_4$/TiO$_2$ samples may be attributed to the effective interfacial charge separation resulted from the fabrication of a heterojunction. However, as the amount of mpg-C$_3$N$_4$ further increases, the degradation rate decreases obviously. This may be attributed to the fact that the thickness of mpg-C$_3$N$_4$ shell is too thick that will shield UV light off TiO$_2$, which lead to decreasing the photocatalytic activity. The photocatalytic decomposition of MB by different catalysts was generally in accordance with first-order kinetics. The corresponding apparent rate constants are shown in Fig. 6(c). The mpg-C$_3$N$_4$/TiO$_2$–3% has the highest apparent rate constant of 2.05 h$^{-1}$, which was about 4.1 times as that of pure anatase TiO$_2$ sample (0.50 h$^{-1}$) and 5.6 times as that of P25 (0.36 h$^{-1}$). The results suggest that there is a significant synergistic effect between TiO$_2$ and mpg-C$_3$N$_4$ for photocatalyzed degradation of MB under UV light irradiation.

Fig. 6(b) shows the photocatalytic activities of the mpg-C$_3$N$_4$/TiO$_2$ samples under visible light irradiation. Except the mpg-C$_3$N$_4$/TiO$_2$–1%, all the mpg-C$_3$N$_4$/TiO$_2$ photocatalysts exhibit higher photocatalytic activity than mpg-C$_3$N$_4$ sample under visible light irradiation. As shown in Fig. 6(d), the apparent rate constant of mpg-C$_3$N$_4$/TiO$_2$–6% is 0.21 h$^{-1}$, which is 2.76 times higher than that of mpg-C$_3$N$_4$ (k = 0.075 h$^{-1}$). Different from the UV activity, the mass ratios of mpg-C$_3$N$_4$/TiO$_2$ with the highest apparent rate constant under visible light irradiation (6%) is higher than that under UV light irradiation (3%). The reason is that the visible activities for mpg-C$_3$N$_4$/TiO$_2$ samples are due to the excitation of mpg-C$_3$N$_4$. Increasing the ratios of mpg-C$_3$N$_4$ will benefit to enhance the visible light absorption. So the activity order for mpg-C$_3$N$_4$/TiO$_2$ samples under visible light is different from that under UV light.

The comparison of decolorization and mineralization at different time intervals under UV and visible light irradiation are shown in Fig. 7(a) and (b). Compared with the decolorization process, mineralization is slower: 53% of the organic content of MB was degraded in 2 h of the reaction time for mpg-C$_3$N$_4$/TiO$_2$–3% under UV light irradiation, while the corresponding decolorization was almost 100%. In comparison to 64% decolorization in 6 h of the reaction time for mpg-C$_3$N$_4$/TiO$_2$–6% under visible light irradiation, only 21% of TOC was eliminated in the same period. The disagreement between the two measurements suggests that, the oxidizing species interact with the giant dye molecules to split it into smaller intermediates, thus causing the fragmentation of dye with significant damages to the conjugated structure that results in the decolorization of dye, while the degradation products of the dyes are certainly still present in the solution. Hence, the mineralization process is slower than decolorization.

![Fig. 4](image) The nitrogen adsorption–desorption isotherms (a) and corresponding curve of the pore size distribution (b) for TiO$_2$, mpg-C$_3$N$_4$ and mpg-C$_3$N$_4$/TiO$_2$.

![Fig. 5](image) UV-vis diffuse reflection spectra of TiO$_2$, mpg-C$_3$N$_4$ and mpg-C$_3$N$_4$/TiO$_2$ composites.
As reported by literatures,\textsuperscript{39,40} the dye sensitization always contributes a lot to dye degradation. To well study the photocatalytic activity of mpg-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} under visible light, colorless 2,4-dichlorophenol was also chosen as the model pollutant. Fig. 8 shows the data for the degradation and mineralization of 2,4-dichlorophenol (after reacted for 12 h) over P25, anatase TiO\textsubscript{2}, mpg-C\textsubscript{3}N\textsubscript{4} and mpg-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} - 6\% under visible light irradiation. As it can be observed, the best performance was obtained with the mpg-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} - 6\% catalyst since the degradation and mineralization percentages under visible light irradiation are higher than those obtained with P25, anatase TiO\textsubscript{2} and mpg-C\textsubscript{3}N\textsubscript{4}, which also suggests that the dye sensitization is not the main cause of dye degradation.

The comparative studies of the photocatalytic activity of the prepared mpg-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} with that of photocatalysts in literature\textsuperscript{8,23,24,32,41} are shown in Table 1. The data in Table 1 show that other experiments have the same rules: the photocatalytic activity of photocatalysts firstly increased and then decreased with increasing the mass ratios of C\textsubscript{3}N\textsubscript{4}. On the other hand, the mass ratios of C\textsubscript{3}N\textsubscript{4} with the highest apparent rate constant under visible light irradiation is higher than that under UV light irradiation. Compared with other synthetic method, ultrasonic dispersion method is more facile and convenient. And the synthetic mpg-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} composites have high stability, which has been proved by the following circulation experiments of MB degradation.

The stability of the as-synthesized mpg-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} sample was evaluated by the circulation experiments. From Fig. 9(a), it can be observed that the as-prepared mpg-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} - 3\% maintained a stable and high photocatalytic activity except for about 2.97\% decrease in photocatalytic efficiency after 3 recycling runs for the photodegradation of MB under UV light irradiation. In Fig. 9(b), the photocatalytic activity of the mpg-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} - 6\% sample has no apparent deactivation (9.06\%) after three recycles for the degradation of MB under visible light irradiation, indicating that the TiO\textsubscript{2}/mpg-C\textsubscript{3}N\textsubscript{4} composites can serve as a stable and efficient photocatalyst.

In order to evaluate the photocatalytic degradation of different dyes by the as-synthesized TiO\textsubscript{2}/mpg-C\textsubscript{3}N\textsubscript{4} composite, MO and RhB were also chosen as the model dye. Fig. 10 clearly shows that the photocatalytic degradation efficiency decreases in the order: RhB > MB > MO. As we know, MB and RhB are cationic dyes and MO is an anionic dye. Because the TiO\textsubscript{2}/mpg-C\textsubscript{3}N\textsubscript{4} product inherits negative surface charge, the cationic dye (MB and RhB) can be easily absorbed onto the catalyst surface by the electrostatic field force, and charge transfer is facilitated. But for the anionic dye (MO), this effect is not operative as such. So, it is easily understood that the degradation efficiency of MO.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.png}
\caption{Photocatalytic degradation curves and apparent rate constants for the photocatalytic degradation of MB over P25, TiO\textsubscript{2}, mpg-C\textsubscript{3}N\textsubscript{4} and mpg-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} composites under UV light irradiation (a and c) and under visible light irradiation (b and d).}
\end{figure}
lower than that of MB and RhB. As a cationic dye, RhB contains a carboxyl group that can be hydrolyzed to release H⁺. However, the hydrolyzed MB is endowed with a negative charge due to the COO⁻/COOH groups, thus different adsorption could occur between them. As a result, the degradation efficiency of RhB is higher than that of MB. Therefore, it is the molecular structure and the charge properties of the dyes that lead to different degradation efficiencies.

3.3. Mechanism of photocatalytic activity enhancement

In order to directly observe the separation rate of photo-induced electron–hole pairs over different samples, PL spectrum analysis were carried out, which can directly offer information for the separation or recombination efficiency of photo-generated charge carriers. The higher the recombination rate of photogenerated e⁻ and h⁺ is, the higher intensity the PL spectra display. Fig. 11 shows the PL spectra of the pure anatase TiO₂, pure mpg-C₃N₄ and mpg-C₃N₄/TiO₂ composites. The mpg-C₃N₄/TiO₂ photocatalysts exhibit the emission peaks locating at almost the same position with the pure anatase TiO₂, but decreased emission intensities, which suggested that the recombination of photogenerated charge carriers was greatly inhibited in the mpg-C₃N₄/TiO₂. This reason might be that the heterojunction formed at interface between anatase TiO₂ and mpg-C₃N₄ can prevent the recombination of photogenerated charge effectively.

During the photocatalytic oxidation process, the ‘O₂⁻, h⁺ and ‘OH all can serve as active species and play important roles in the degradation process of organic dyes. In order to determine the dominant active radicals and reveal the photocatalytic mechanism, the active species trapping experiments were carried out. As shown in Fig. 12(a), the photocatalytic degradation efficiency of MB was significantly depressed when the system is replenished with N₂ or added EDTA-2Na, showing that ‘OH has minor effect on the degradation of MB. It is also seen that the photocatalytic degradation of MB was almost not affected by the addition of TBA, which indicates that ‘OH has minor effect on the degradation of MB. It can be observed from Fig. 12(b) that there is almost no influence when TBA and EDTA-2Na were added, suggesting that ‘OH and h⁺ are not the main active species. However, the degradation behavior of MB was significantly decreased when the system is replenished with N₂. It reveals that the superoxide radicals (‘O₂⁻) are the main active species for MB degradation under visible light irradiation.

On the basis of the above optical property analysis and active species trapping experiments, the possible photocatalytic mechanism of the mpg-C₃N₄/TiO₂ composites under UV and visible light could be proposed in Fig. 13(a) and (b), respectively. First, as illustrated by SEM and HRTEM, the surfaces of the TiO₂ microspheres is a mosaic structure which covered with interconnected square nanoflakes, and the exposed surface is (001) facets. As can been seen in Fig. 13(a), anatase TiO₂ can absorb UV light to produce the photogenerated electron–hole pairs.
The photogenerated electrons tend to be transported to the \{101\} facet with higher positive surface potential, and are easier to react with oxygen molecules to generate active species superoxide radical ('$O_2^-$') for the degradation of dyes. The photogenerated holes tend to be transported to the \{001\} facet with lower positive surface potential.\textsuperscript{46,47} Meanwhile, the holes on TiO$_2$ could easily transfer to mpg-C$_3$N$_4$, since the valence band (VB) position of TiO$_2$ (2.7 eV) is lower than that of mpg-

<table>
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<th>Samples</th>
<th>Method</th>
<th>Experimental content</th>
<th>Highest UV activity</th>
<th>Highest visible activity</th>
<th>Ref.</th>
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<tr>
<td>g-C$_3$N$_4$-P25</td>
<td>Calcination</td>
<td>0–56%</td>
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<td>g-C$_3$N$_4$/TiO$_2$</td>
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<td>11.3%</td>
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<td>8</td>
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<tr>
<td>ZnO@mpg-C$_3$N$_4$</td>
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<td>4%</td>
<td>20%</td>
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<tr>
<td>C$_3$N$_4$/BiPO$_4$</td>
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<td>4%</td>
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<tr>
<td>BiOCl-C$_3$N$_4$</td>
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<tr>
<td>mpg-C$_3$N$_4$/TiO$_2$</td>
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<td>0–20%</td>
<td>3%</td>
<td>6%</td>
<td>Present paper</td>
</tr>
</tbody>
</table>

Fig. 9  Cycling runs of mpg-C$_3$N$_4$/TiO$_2$ composite for the degradation of MB by mpg-C$_3$N$_4$/TiO$_2$–3% under UV light irradiation (a) and mpg-C$_3$N$_4$/TiO$_2$–6% under visible light irradiation (b).
C₃N₄ (1.62 eV).48,49 And the photogenerated holes could transfer dyes to its intermediates or directly to CO₂ and H₂O. Because of the high exposed {001} facets of anatase TiO₂ and the hetero-junction structure between TiO₂ and mpg-C₃N₄, the recombination of photoinduced charge carriers was inhibited. As a result, the photocatalytic activity is significantly increased. The supposed photocatalytic mechanism was also in good agreement with the result from the active species trapping experiments. Fig. 13(b) gives a possible schematic mechanism of the visible light activity. Anatase TiO₂ cannot be excited under visible light irradiation. While mpg-C₃N₄ can absorb the visible light to induce \( p^-p^* \) transition and transport the excited-state electrons from the VB to the CB. The CB potential of mpg-C₃N₄ (1.12 eV) is more negative than the CB edge of anatase TiO₂ (0.5 eV), so the excited electron on mpg-C₃N₄ could directly inject into the CB of anatase TiO₂. These electrons would subsequently transfer to the surface of photocatalyst to react with oxygen to form superoxide radicals for the...
degradation of dyes. Therefore, the hybrid effect and energy level match between two semiconductors are two key factors for the effective separation of photogenerated electron–hole pairs.

4. Conclusion

In summary, mpg-C$_3$N$_4$/TiO$_2$ with reactive {001} facets composites were synthesized via a facile ultrasonic dispersion method and the effects of mass ratios of mpg-C$_3$N$_4$/TiO$_2$ + mpg-C$_3$N$_4$ on photocatalytic activity of mpg-C$_3$N$_4$/TiO$_2$ composites were investigated. The results revealed that the mpg-C$_3$N$_4$/TiO$_2$–3% has the highest photocatalytic activity under UV light irradiation, which was about 4.1 times as that of pure TiO$_2$ sample and 5.6 times as that of P25. The mpg-C$_3$N$_4$/TiO$_2$–6% has the highest photocatalytic activity under visible light irradiation, which was about 2.76 times as that of mpg-C$_3$N$_4$. Compared with the decolorization process, mineralization is slower. The degradation of 2,4-dichlorophenol suggests that the dye sensitization is not the main cause of dye degradation. After 3 recycling runs for the photodegradation of MB, high photocatalytic performance of the mpg-C$_3$N$_4$/TiO$_2$ composites was effectively maintained. The photocatalytic degradation efficiency of different dyes was found to be in the decreasing order of RhB > MB > MO. The radical trapping experiments demonstrate that the active species involved in the photocatalytic degradation reaction under UV light irradiation are super oxide radicals (’O$_2^-$) and holes (h$^+$), while superoxide radicals (’O$_2^-$) serving as the main active species under visible light irradiation. The excellent photocatalytic performance should be attributed to the reduced recombination rate of photogenerated electrons and holes, which stems from the {001} facets of TiO$_2$ and the heterojunction formed at interface between anatase TiO$_2$ and mpg-C$_3$N$_4$.

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References


