

Characterization and photocatalytic activity of N and Pt doped titania prepared by microemulsion technique

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Abstract

N and Pt doped titania ($\text{Pt/TiO}_{2-x}\text{N}_x$) nanoparticles were prepared by the microemulsion method. The as-prepared products were characterized by using X-ray photoelectron spectroscopy, nitrogen adsorption-desorption, and transmission electronic microscopy. Results reveal that the photocatalysts possess a particle size of 4-8 nm with a specific surface area of 130-160 m^2/g and exhibit a narrow pore size distribution and high total pore volume. The effect of Pt loading content on the photocatalytic activity was investigated. The degradation of methylene blue over as-prepared titania in aqueous solution under visible light irradiation was remarkably enhanced by codoping N and Pt elements.

Introduction

In photocatalysis, TiO_2 is the most attractive semiconductor among transition metal oxides because of its excellent performance in photocatalytic reactions [1-4]. TiO_2 has also been widely used as a photocatalyst in waste air and wastewater treatment due to its relatively high photocatalytic activity, chemical stability, nontoxicity, low cost, and environmentally friendly property [1,3,5-7]. However, TiO_2 with a band gap of ca. 3.2 eV can be photoexcited under irradiation of UV light ($\lambda < 395 \text{ nm}$), which is less than 5 % of sunlight. Therefore, considerable effort has been made to increase the absorption of TiO_2 in the visible region to improve its visible light response through various modifications such as doping of various metal, metal oxides or nonmetal. Recently, N-doped TiO_2 has been studied by many researchers [8-12] and demonstrated its photoactivity for decomposition of many organic compounds under visible light irradiation.

If the light energy is equal to or greater than the bandgap of the semiconductor, the electron in the valance band can be excited to the conduction band. This energy change will result in the formation of positive holes in the valance and free electrons in the conduction band. However, the positive hole and electron are easily recombined in a very short time, which will therefore lead to a very low activity for the photocatalyst. The loaded platinum on the surface of TiO_2 can play an important role in preventing the rapid recombination between positive hole and electron. It is because the platinum can capture the transferred electrons onto the surface of the TiO_2 [1,13].

The importance of nanophase technology has resulted in tremendous research efforts towards the development of new techniques for the synthesis of nanosized particles. One such technique with the ability to precisely control the size and shape of the particles formed was to use water-in-oil microemulsions as a reaction medium. The aqueous cores/water pools of these microemulsions can be used as nanosize reactors for the precipitation of a wide variety of nanoparticles. Compared to other methods, the microemulsion method has several advantages in producing high-purity particles with uniform small size, narrow size distribution, and low aggregation properties [14-16].

Accordingly, the N and Pt doped titania ($\text{Pt/TiO}_{2-x}\text{N}_x$) photocatalysts in this work were prepared by using the microemulsion method, their characterizations by X-ray photoelectron spectroscopy (XPS), nitrogen adsorption-desorption analysis, and transmission electronic microscopy (TEM) were relatively described. The photocatalytic activities of the as-prepared photocatalysts were evaluated by degrading methylene blue under visible light irradiation (as a model reaction). The effect of Pt loading content on the photoactivity was also studied.

Materials and methods

Materials

n-hexane ($\geq 99 \%$ purity, Acros), citric acid monohydrate ($\geq 99.5 \%$ purity, Riedel-de Haën), titanium(IV) isopropoxide (TIP, 98 % purity, Fluka), ammonia solution (15 M, Showa), hydroxypropyl cellulose (HPC, m. w. = 100,000, Aldrich), potassium hexachloroplatinate (99 % purity, Showa), sorbitan monopalmitate (Span 40, HLB = 6.7, Sigma), and isopropyl alcohol (IPA, $\geq 99.5 \%$ purity, ECHO) were used for this study. All chemicals were used without further purification. Span 40 and IPA were used as a surfactant and cosurfactant respectively. HPC behaved as a steric dispersant. Citric acid serving as a modifying agent was applied to moderate the hydrolysis and condensation processes of titanium precursor.

Preparation of $\text{Pt/TiO}_{2-x}\text{N}_x$ photocatalysts

Nanosized $\text{Pt/TiO}_{2-x}\text{N}_x$ powders were synthesized by the microemulsion method (Figure 1). Both the oil phase (continuous

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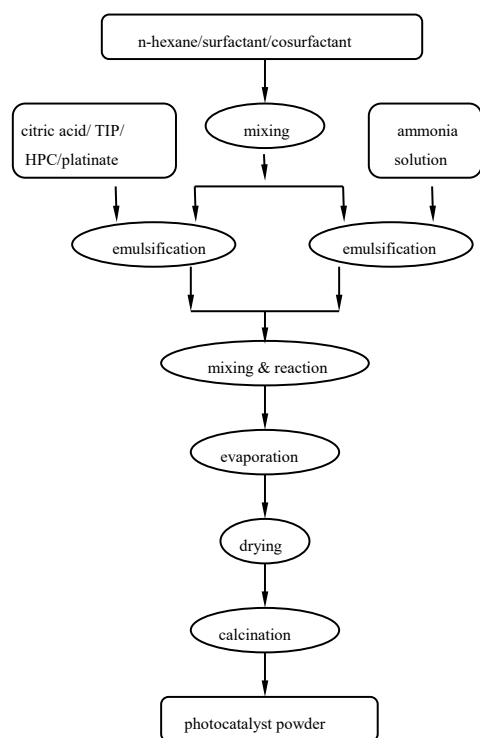


Figure 1. Preparation of Pt/TiO_{2-x}N_x photocatalyst powders using the microemulsion method

phase) of the each microemulsion were composed of n-hexane, Span 40, and IPA. The two solutions of microemulsion, one contained 5.0×10^{-5} M hydroxypropyl cellulose, citric acid / titanium isopropoxide with molar ratio 3, and a necessary amount of potassium hexachloroplatinate for desired Pt loading of 0–0.7 wt% aqueous droplets, the other contained aqueous ammonia droplets with the same volume ratio of water/oil (w/o) at 1/100, were mixed together and kept continuously stirring at 50 °C for 1 h to form a milky slurry of titania precursor. After the consecutive procedures of evaporation, drying, calcination at 500 °C, and grind, the desired photocatalysts were obtained.

Characterization of photocatalysts

The surface area of the Pt/TiO_{2-x}N_x powders was determined by a BET analyzer (Micromeritics, ASAP 2101), and the surface structure and particle morphology were examined by a transmission electronic microscopy (TEM) (Philips, CM-200). The surface composition and bonding of the Pt/TiO_{2-x}N_x powders were detected by X-ray photoelectron spectroscopy (XPS) (Ulvac-Phi, Model ES 650). The binding energy was referenced to the C1s line at 284.6 eV for calibration.

Photocatalytic activity experiments

The photocatalytic activity experiments on Pt/TiO_{2-x}N_x powders for the photodegradation of a dye in water were carried out in a Pyrex glass reactor under visible light irradiation. Analytical grade methylene blue was used as the model dye chemical. Its aqueous suspension was prepared by adding 0.2 g of photocatalyst powder to 300 mL of 10 ppm aqueous methylene blue solution. The visible light irradiation was provided by a high-pressure mercury lamp and an appropriate cutoff filter was placed in the front of the reactor to remove the part of UV radiation. At given irradiation time intervals, samples of 5 mL volume were taken from the suspension and immediately centrifuged at 5000 rpm for 10 min, then passed through a 0.45 µm Millipore filter

to remove the particles. The concentration of methylene blue was measured at the maximum absorption wavelength of 664 nm by a UV-Vis spectrophotometer.

Results and discussion

Characterization of Pt/TiO_{2-x}N_x catalyst

The morphology of the as-synthesized Pt/TiO_{2-x}N_x powders was examined by TEM (Figure 2). The Pt/TiO_{2-x}N_x particles were clearly observed with a typical size of 4–8 nm.

The Brunauer-Emmett-Teller (BET) gas adsorption method has become the most widely used standard procedure for the determination of the surface area of finely-divided and porous materials. Figure 3 shows the nitrogen adsorption–desorption isotherms of the TiO_{2-x}N_x and 0.6 wt% Pt/TiO_{2-x}N_x prepared by microemulsion method. The isotherms exhibit typical Type IV pattern with hysteresis loop, characteristic of mesoporous material according to the classification of IUPAC [17]. A sharp increase in adsorption volume of N₂ was observed and located in the P/P₀ range of 0.45–1.00. This sharp increase can be attributed to the capillary condensation, indicating the good homogeneity of the sample. As can be seen from figure 4, the pore size distributions obtained by BJH approach are noticeably narrow, confirming good quality of the samples. It is found that the mean pore diameter of the TiO_{2-x}N_x photocatalysts is obviously decreased with the increased amount of Pt loading. The textural properties of the photocatalysts prepared by microemulsion method are given in table 1. The higher the Pt content was loaded, the larger the decrease in the BET surface area of the samples was observed. The mean pore diameter and the total pore volume of the photocatalysts decreased in similar trend to the surface area. It may be concluded that such the small amount of Pt loaded disturbed the mesopore volume by depositing at the surface of the TiO_{2-x}N_x aggregates, while maintaining the general pore size characteristic. By comparison, the BET surface area of the synthesized samples are quite higher than that of Degussa P-25 (a commercial TiO₂ photocatalyst), which is widely used in photocatalysis. It is concluded that Pt/TiO_{2-x}N_x prepared by microemulsion method in this work has the advantage of giving high specific surface area. It should be good for the photocatalytic reaction.

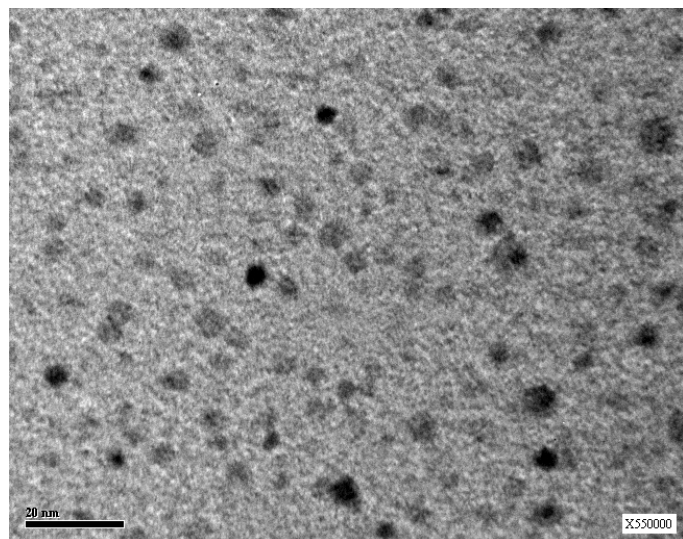
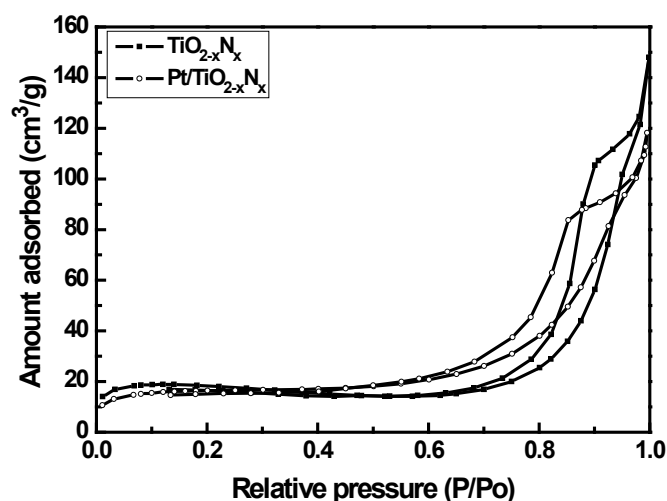
The surface composition and bonding of the as-synthesized Pt/TiO_{2-x}N_x powders were analyzed by X-ray photoelectron spectroscopy (XPS). Figure 5 shows the XPS signals over the whole scanned energy range (0–1100 eV). As seen, the presence of Ti 2p, O 1s, N 1s and Pt 4f signals in the spectra of the sample demonstrated the as-synthesized powders consist of Ti, O, N, and Pt elements. Figures 6–9 show the high-resolution Ti 2p, O 1s, N 1s and Pt 4f spectra of the Pt/TiO_{2-x}N_x powders.

The Ti 2p XPS peaks of the pure TiO₂ appeared at 458.2 eV and 464.0 eV for Ti 2p_{3/2} and Ti 2p_{1/2}, respectively [18]. For the as-synthesized powders, the Ti 2p_{3/2} and Ti 2p_{1/2} peaks shifted to 457.2 eV and 463.1 eV (not shown), respectively. The lower binding energy of the Ti 2p should be attributed to the incorporation of substitutional N into TiO₂ lattice [19,20]. In figure 6, the Ti 2p_{3/2} peak can be fitted into two Gaussian peaks at 457.4 and 456.9 eV, respectively. The former is attributed to the Ti⁴⁺ on the surface; the latter is ascribed to the Ti³⁺ on the surface. It is clear that the presence of Ti³⁺ arose from the depositing of Pt on the surface of TiO₂ [21].

The N 1s XPS spectrum of the as-synthesized powders showed a broad peak that could be deconvoluted into two peaks, as shown in figure 7. The binding energies centered at 400.0 and 397.2 eV were

Table 1. Textural properties of photocatalysts from N₂ adsorption - desorption analysis

Photocatalyst	BET surface area	Mean pore diameter	Total pore volume
	(m ² g ⁻¹)	(nm)	(cm ³ g ⁻¹)
TiO _{2-x} N _x	158.2	9.5	0.332
0.1 wt%Pt/TiO _{2-x} N _x	157.6	9.3	0.303
0.6 wt%Pt/TiO _{2-x} N _x	135.1	7.8	0.259
P-25	48.0	12.6	0.120

**Figure 2.** TEM image of 0.2 wt% Pt/TiO_{2-x}N_x prepared by microemulsion method**Figure 3.** N₂ adsorption - desorption isotherms of TiO_{2-x}N_x and 0.6 wt% Pt/TiO_{2-x}N_x

assigned to molecularly chemisorbed nitrogen γ -N₂ and substitutional nitrogen β -N [12,22-23], respectively. The β -N species were nitrogen interacting with Ti through Ti-N bond formation and contributed to the band-gap narrowing which lead to a significant red shift of the absorption edge to the visible-light region [20]. Using the Gaussian fitting and quantitative analysis, the relative percentage of the two N species are 58.6 % and 41.4 % for β -N and γ -N₂, respectively. It is revealed the substitutional nitrogen is more than the chemisorbed nitrogen on the surface of the as-prepared powders.

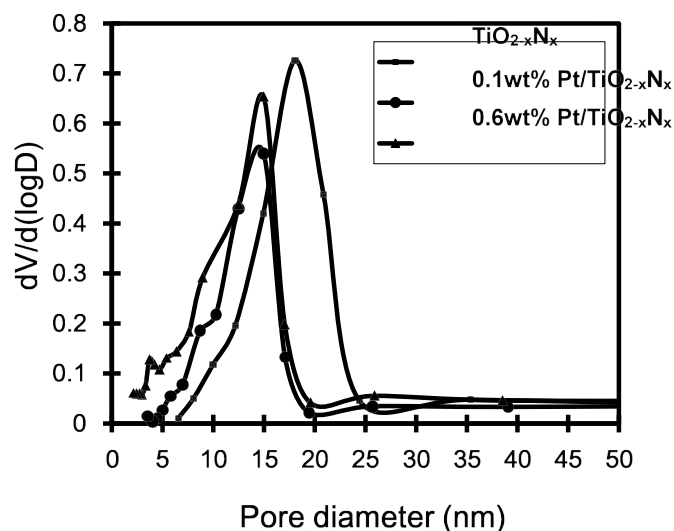
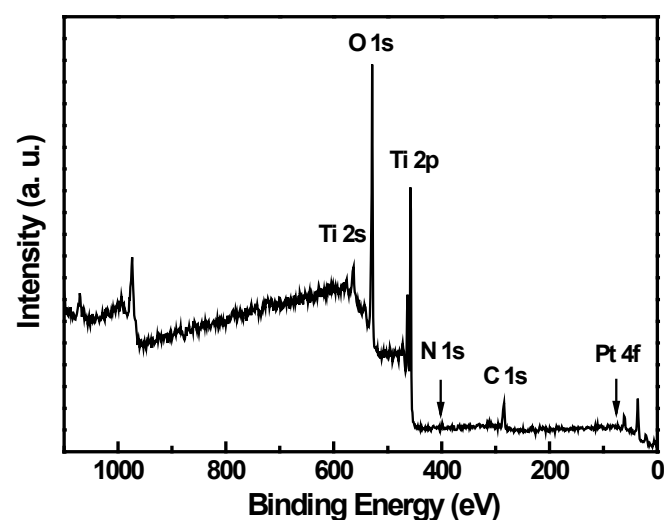
According to the reports [18,24-27], the typical O 1s electron binding energy for TiO₂ molecule is 529.3 eV. Figure 8 shows the O 1s spectrum of Pt/TiO_{2-x}N_x centered at 528.5 eV. In this case, the

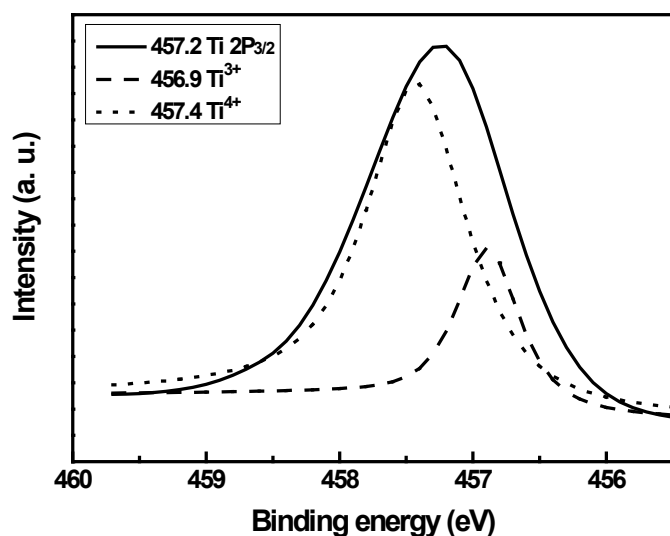
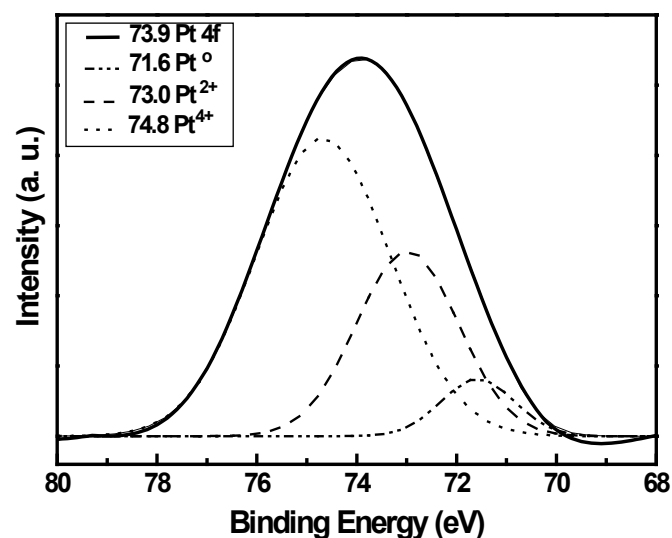
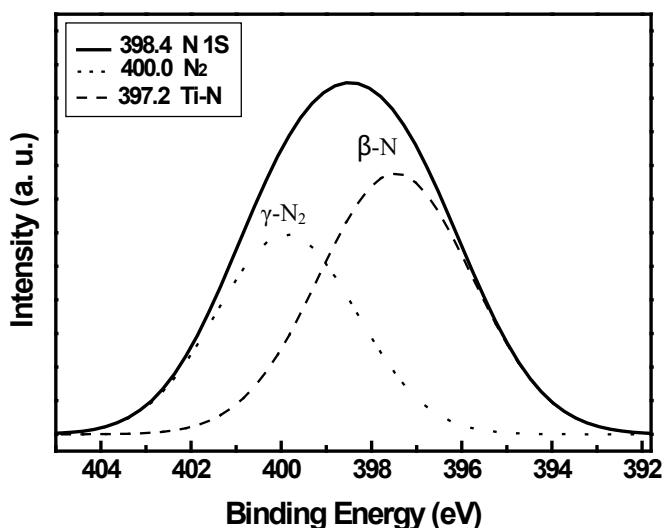
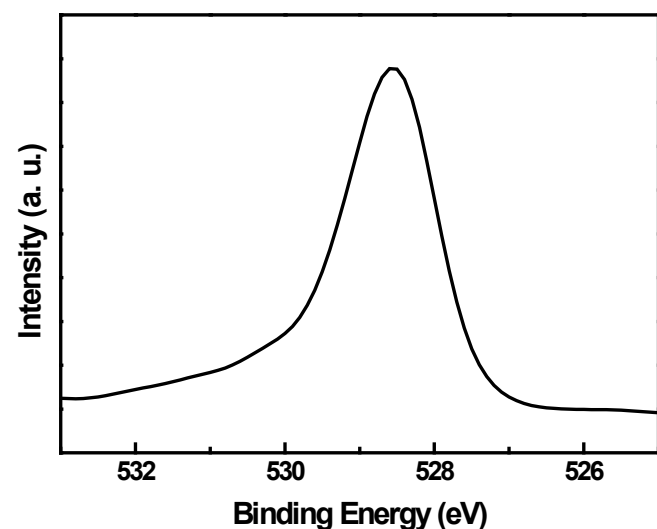
binding energy was shifted to a lower value, which could be due to the substitutional N-doping into TiO₂ lattice and affected the binding energy of the O 1s peak.

In figure 9, the Pt 4f peak of Pt/TiO_{2-x}N_x consisted of three individual peaks, corresponding to metallic Pt, PtO, and PtO₂, respectively. The peak at 71.6 eV can be attributed to metallic Pt, the peaks at 73.0 eV and 74.8 eV can be assigned to Pt oxides PtO and PtO₂, respectively. The different species of Pt on the surface of TiO_{2-x}N_x have different photoactivity and optical absorption properties. Therefore, the photosensitization of Pt/TiO_{2-x}N_x samples to visible light was partially caused by the presence of Pt, PtO, and PtO₂ on the surface of TiO_{2-x}N_x. Using the Gaussian fitting and quantitative analysis, the relative percentage of the three Pt species are 6.7 %, 30.0 %, and 63.3 % for Pt, PtO, and PtO₂, respectively. The XPS results revealed that PtO₂ is the predominant species on the TiO_{2-x}N_x surface.

Photocatalytic activity

Methylene blue (MB), an organic dye, was selected as target compound because MB is ubiquitously used and the removal of the dye

**Figure 4.** Pore size distributions of Pt/TiO_{2-x}N_x at various Pt loadings**Figure 5.** XPS spectrum of the Pt/TiO_{2-x}N_x powders

Figure 6. Ti 2p XPS spectrum of the Pt/TiO_{2-x}N_x powdersFigure 9. Pt 4f XPS spectrum of the Pt/TiO_{2-x}N_x powdersFigure 7. N 1s XPS spectrum of the Pt/TiO_{2-x}N_x powdersFigure 8. O 1s XPS spectrum of the Pt/TiO_{2-x}N_x powders

from wastewaters has been an acute problem [28]. The photocatalytic activity of the Pt/TiO_{2-x}N_x was quantitatively examined by photocatalytic degradation of methylene blue in water for 24 h irradiation using visible light. As can be seen from figures 10 and 11, the concentration of methylene blue decreased with increasing the irradiation time. The activity of Pt/TiO_{2-x}N_x with Pt loading in the range of 0.1–0.6 wt% is much higher than that of TiO_{2-x}N_x (0 wt% Pt) and the commercial TiO₂ photocatalyst P-25 in the methylene blue degradation. An optimum content of Pt impurity was 0.2 wt%, and any lower or higher content of Pt impurity was detrimental to the advancement of photoactivity. The presence of Pt on TiO_{2-x}N_x favors the migration of photogenerated electron to platinum thus improving the electron–hole separation. On the basis of the relevant band positions of Pt and TiO_{2-x}N_x, Pt clusters at a lower concentration act as a separation center. The photogenerated electrons are transferred from TiO_{2-x}N_x conduction band to the Pt conduction band and the holes accumulate in the TiO_{2-x}N_x valence band. Hence, photogenerated electrons and holes were efficiently separated. However Pt clusters at a higher concentration act as a recombination center and the recombination rate between electrons and holes increases exponentially with the increase of Pt concentration because the average distance between trap sites decreases by increasing the number of Pt clusters confined within a particle [21]. Furthermore, too much Pt clusters on TiO_{2-x}N_x would shield the photosensitive TiO_{2-x}N_x surface, scatter the visible light to decrease the absorption by TiO_{2-x}N_x and subsequently decrease the surface concentration of the electrons and holes available for further reactions.

Conclusion

Nanosized Pt/TiO_{2-x}N_x photocatalysts with a typical size of 4–8 nm were prepared by the microemulsion method. XPS analysis revealed the existence of Pt⁰, Pt²⁺, and Pt⁴⁺ species on the surface of the Pt/TiO_{2-x}N_x and nitrogen interacting with Ti through Ti–N bond formation. Both the Pt-doping and substitutional N contribute to the response to visible light. The pore size distributions are noticeably narrow, indicating the good homogeneity of the as-prepared powders. The specific surface area and total pore volume of the as-prepared powders are much higher than that of commercial TiO₂ photocatalyst P-25 (Degussa), which is beneficial to increase the opportunities of contacts between photocatalysts and dyes in water, resulting in high efficiency of destruction for dye compounds. The photocatalytic degradation of MB

dye in aqueous solutions under visible light irradiation was promoted with doping an appropriate amount of Pt on the $\text{TiO}_{2-x}\text{N}_x$ surface. The optimal content of Pt was found to be 0.2 wt%.

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