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Article

Robust photocatalytic benzene degradation using mesoporous disk-like N-TiO₂ derived from MIL-125(Ti)

Chen Zhao ^{a,b}, Zhihua Wang ^{a,*}, Xi Chen ^b, Hongyu Chu ^b, Huifen Fu ^b, Chong-Chen Wang ^{b,#}^a State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China^b Beijing Key Laboratory of Functional Materials for Building Structure and Environment Remediation, Beijing University of Civil Engineering and Architecture, Beijing 100044, China

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ABSTRACT

N-doped anatase-rutile titanium dioxide (N-TiO₂) is a classical semiconductor widely used in environmental remediation. Its photocatalytic performance is typically affected by its morphology, porous structure, and phase composition. Herein, disk-like mesoporous N-TiO₂ was prepared by calcining MIL-125(Ti) and melamine matrix at different temperatures in air. The photocatalytic efficiency of the prepared mesoporous N-TiO₂ for the photo-oxidation of gaseous benzene under visible-light irradiation was studied. With respect to light absorption and mass transfer, as-prepared N-TiO₂ annealed at 500 °C (MM-500) showed the best photocatalytic activity with corresponding photodegradation and mineralization efficiencies of 99.1% and 72.0%, respectively. In addition, MM-500 exhibited excellent reusability and stability in cyclic experiments, in which 84.8% of gaseous benzene could still be photodegraded after 10 experimental cycles. Furthermore, electron spin resonance analysis indicated that •OH and •O₂⁻ radicals were the dominating reactive oxygen species during the photo-oxidation process. Their excellent performance suggests that the as-prepared N-TiO₂ photocatalysts can be used to eliminate volatile organic compounds.

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1. Introduction

Benzene is a common volatile organic compound (VOC) and exposure to it might cause a variety of diseases in human beings, such as aplastic anemia, leukemia, and multiple myeloma [1–3]. Therefore, there is an urgent need for a highly efficient method to eliminate gaseous benzene. According to previous reports [4,5], heterogeneous photocatalytic oxidation (PCO) using semiconductors is a powerful VOC-removal method. Be-

cause of its unique characteristics and environmental friendliness, TiO₂ is an efficient and commonly used photocatalyst for degrading different types of VOC contaminants [6–8]. However, the main drawbacks of TiO₂ are its relatively large bandgap (the *E_g* values of anatase and rutile phases are 3.2 and 3.0 eV, respectively) and a high recombination rate of photo-induced electron-hole pairs, which limit its applications in visible-light or real sunlight irradiation [9–11]. In order to harness the rest of the solar spectrum for TiO₂ applications, great efforts have

* Corresponding author. E-mail: zhwang@mail.buct.edu.cn

Corresponding author. E-mail: wangchongchen@bucea.edu.cn

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been put in to the fabrication of visible-light-responsive TiO₂ doped with non-metallic elements, such as boron (B) [12,13], sulfur (S) [14,15], carbon (C) [16,17], fluorine (F) [18,19], and nitrogen (N) [9,20–22]. Compared to other non-metals, N-doped TiO₂ (N-TiO₂) photocatalysts exhibit a superior photocatalytic performance and strong absorption ability in different reactions when irradiated by visible light [5].

Recently, a large number of synthetic methods have been reported for the fabrication of N-TiO₂ photocatalysts, such as the calcination of pure TiO₂ in a gaseous NH₃ atmosphere [23,24], direct oxidation of TiN [25,26], treating mixtures of TiO₂ and urea [27,28], sputtering of TiO₂ in a gaseous N₂ atmosphere [29], and hydrothermal treatment of Ti-containing precursors with an NH₃ solution [22,30]. However, the photocatalytic performance of N-TiO₂ is typically affected by several factors, such as its morphology, phase composition, pore structure, crystal size, and specific surface area. For example, previous studies suggested that an appropriate ratio of anatase and rutile phases is beneficial for improving the photocatalytic activity of TiO₂ as it would reduce the rate of photo-induced electron-hole recombination [31,32]. Nevertheless, TiO₂-based photocatalysts are limited in the photodegradation of aromatic organic pollutants, such as benzene, owing to their deactivation behavior [1,5]. Therefore, to increase the photon-absorption capacity of the catalysts and accelerate the transfer of intermediates, it is imperative to design new types of N-TiO₂ with a specific morphology and microstructure.

Metal-organic frameworks (MOFs), which are porous crystalline multi-functional materials, are attracting increasing attention due to their ultra-high specific surface area and tunable structure [33–36]. In view of the fact that the open channels and abundant nano-sized cavities in MOFs are beneficial to the release and transport of intermediates during photocatalytic processes, MOFs are regarded as the ideal precursors or templates for the preparation of porous metal oxides (PMOs) [37–40]. Because the arrangement of metallic elements and oxygen inside MOF crystals follows a periodical atomic level, PMOs can be fully transformed from MOFs without long-range atomic migration, thus preserving the porosity of MOFs after derivative treatments. For example, porous tube-like ZnO nanoparticles can be fabricated using a mild preparation method using ZIF-L as the self-sacrificing precursor [41]. Spindle-like mesoporous Fe₂O₃ nanoparticles were produced by the pyrolysis of MIL-88(Fe) [42]. A facile synthesis method has been developed for Cu/Cu₂O/C composites using an aldehyde resin as the carbon source and HKUST-1 as the sacrificial template [43]. As a representative Ti-containing MOF, MIL-125(Ti) was firstly prepared by Dan-Hardi and co-workers [44]. Several researchers fabricated porous TiO₂ or TiO₂/C materials via the pyrolysis of MIL-125(Ti) for application in solar cells and lithium-ion batteries [45–47]. Li et al. [48] constructed cake-like N-TiO₂ by the two-step pyrolysis of MIL-125(Ti) in air and ammonia atmosphere and it exhibited good photocatalytic activity for Rhodamine B removal. However, thus far, there are no reports on N-TiO₂ with a disk-like morphology, mesoporous structure, and mixed anatase-rutile phases fabricated by the calcination of MIL-125(Ti) and melamine mixtures; our intention is to apply

these materials for the photocatalytic degradation of gaseous VOC pollutants.

In this study, a convenient and controllable method was developed to prepare disk-like mesoporous anatase/rutile mixed phase N-TiO₂ through calcination of a mixture of MIL-125(Ti) and melamine. The photocatalytic efficiency of the resultant material was estimated via the photodegradation of gaseous benzene. Furthermore, the visible-light-response mechanism of catalysts with N-doping at different levels was studied. The as-prepared N-TiO₂ is expected to exhibit superior applicability in the photocatalytic degradation of aromatic VOC pollutants.

2. Experimental

2.1. Preparation of disk-like N-TiO₂ photocatalysts

All chemicals used in this study were of analytical grade and were used as received without further purification. Disk-like mesoporous anatase-rutile mixed phase N-TiO₂ photocatalysts were fabricated according to the procedure illustrated in Figure 1. Firstly, MIL-125(Ti) was synthesized using a solvothermal method as described in a previous study [44]. Secondly, mixed powders of 0.3 g of MIL-125(Ti) and 10.0 g of melamine were ground in a Nanjing Nanda planet-type grinding mill system at 30 Hz for 20 min. Finally, the as-prepared mixtures were annealed at 500, 600, and 700 °C for 300 min at a heating rate of 10 °C min⁻¹. The materials annealed at 500, 600, and 700 °C are denoted as MM-500, MM-600, and MM-700, respectively.

2.2. Photocatalytic activity studies

The photodegradation efficiency of gaseous benzene was evaluated in a home-made in-situ quartz reactor. A LED lamp (100 W, CEL-LED100H) was used as the visible-light irradiation source and the corresponding wavelength-distribution spectrum can be found in Supporting Information Figure S1. A thin layer of the as-prepared catalyst (0.05 g) was distributed uniformly on a quartz plate (5.0 cm × 3.5 cm). A pre-defined amount of liquid benzene (1 μL) was injected into the reaction cell. To achieve adsorption/desorption equilibrium between the photocatalyst and target pollutant, gaseous benzene in the reaction cell was diffused for 60 min using a mini fan under dark conditions. Later, the LED lamp was turned on and the photocatalysis process was initiated (the initial concentration of gaseous benzene was approximately 0.007%). The temperature of the reaction mixture was maintained at (25 ± 1) °C using cooling air. During the photodegradation process, benzene and CO₂ concentrations were monitored using a Tech-comp 456C gas-phase chromatograph equipped with FID and TCD detectors.

3. Results and discussion

3.1. X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR)

The XRD patterns of MM-500, MM-600, and MM-700 are

Fig. 1. Schematic illustration of disk-like mesoporous anatase-rutile TiO_2 prepared by the calcination of MIL-125(Ti) and melamine mixtures.

shown in Figure 2(a). MM-500 and MM-600 exhibited several principal peaks at 25.3° , 37.8° , 48.0° , 55.1° , and 62.7° , corresponding to the (101), (004), (200), (211), and (204) crystal planes of anatase TiO_2 (JCPDS 21-1272), respectively. Meanwhile, the characteristic peaks at 27.4° , 36.1° , 41.2° , 54.3° , 56.6° , and 69.0° were indexed with the (110), (101), (111), (211), (220), and (301) crystal planes of rutile TiO_2 (JCPDS 21-1276), respectively [49,50]. When the calcination temperature was increased to 700°C , the characteristic peaks of the anatase phase of MM-700 weakened when compared to those of MM-500 and MM-600. Previous studies demonstrated that calcination temperature is a predominant factor affecting the phase composition of TiO_2 [20,46,51]. Moreover, N-doping might influence the anatase-to-rutile phase transformation [51] and hence, selecting an appropriate calcination temperature is the key to constructing anatase/rutile mixed phase N- TiO_2 . The XRD patterns displayed no diffraction peaks corresponding to impurities and the high degree of crystallinity in both the phases proved that the as-prepared photocatalysts were indeed mixed anatase-rutile phase structures. Additionally, the theoretical crystalline grain sizes of MM-500, MM-600, and MM-700 were obtained by applying the Debye-Scherrer formula shown in Equation (1),

$$D = \frac{K\lambda}{B \cos \theta} \quad (1)$$

where D is the average crystalline grain size, K is a constant (0.89 in this study), λ is the X-ray wavelength, B is the full width at half-maximum (FWHM) in radians obtained using Jade software, and θ is the scattering angle [52]. The theoretical crystalline grain sizes of MM-500, MM-600, and MM-700 were 21.89, 22.55, and 27.57 nm, respectively, indicating that the crystalline grain size of the as-prepared photocatalysts increased with an increase in calcination temperature. Furthermore, the K-value method was applied to quantify the relative ratio of anatase/rutile phases in the as-prepared photocatalysts [52]; these ratios were found to be 91.09%, 77.28%, and 7.37% for MM-500, MM-600, and MM-700, respectively. This result is consistent with the results of XRD analysis.

FTIR characterization can further confirm the existing N species in the TiO_2 lattice. The FTIR spectra of MM-500, MM-600, and MM-700 are illustrated in Figure 2(b). The absorption peak at 3400 cm^{-1} is assigned to the symmetric and asymmetric stretching of hydroxyl groups ($-\text{OH}$) [53] and the peak at 1630 cm^{-1} corresponds to Ti-O functional groups [54]. Compared to commercial TiO_2 (P-25), a small peak concentrated at 1380 cm^{-1} could be observed in these spectra, which

Fig. 2. (a) XRD patterns and (b) FTIR spectra of MM-500, MM-600, MM-700, and P-25.

may be ascribed to surface-adsorbed NH_3 molecules originating from melamine decomposition [55,56]. Meanwhile, the peaks at 1450 and 1090 cm^{-1} can be ascribed to N atoms incorporated in the TiO_2 structure [57]. These results suggest that high-temperature calcination of MIL-125 and melamine mixtures not only induced the chemisorption of NH_3 molecules on the surface of the as-prepared photocatalysts, but also nitrated the TiO_2 network. Nitridation might occur via the substitution of N atoms in NH_3 molecules with O atoms in TiO_2 , giving rise to O–Ti–N or N–Ti–N species. Additionally, the results of elemental analysis (EA) suggested that the concentrations of N in MM-500, MM-600, and MM-700 were 2.33, 1.83, and 1.75 wt.%, respectively, indicating successful N-doping in the as-prepared materials.

3.2. X-ray photoelectron spectroscopy (XPS)

XPS is an effective technique for analyzing the chemical composition and electron structure of as-prepared materials. As illustrated in Figure 3(a), the characteristic peaks of Ti, C, O, and N were obvious in the survey spectrum of MM-500. The main peaks at 284.6, 286.6, and 288.4 eV in the high-resolution C 1s spectrum of MM-500 could be assigned to C=C, C–C, and C=O bonds, respectively (Figure 3(b)), originating from residual carbon after the calcination of MIL-125 [44,58]. The two distinct peaks at 464.4 and 458.8 eV in the Ti 2p spectrum could be ascribed to $\text{Ti } 2p_{1/2}$ and $\text{Ti } 2p_{3/2}$ (Figure 3(c)), respectively [48,59]. Compared to pristine TiO_2 (the binding energy of $\text{Ti } 2p_{3/2}$ is ~ 459 eV) [60], the corresponding peak of $\text{Ti } 2p_{3/2}$ in MM-500 shifted to a lower binding energy (458.8 eV), revealing that N might be embedded in the TiO_2 structure. Typically, the electronegativity of N atoms is lesser than that of O atoms,

which results in a partial electron transition from N to Ti, thus increasing the electron density of Ti atoms. This result further proves that O atoms were replaced by N atoms in the TiO_2 lattice [21,61]. As depicted in Figure 3(d), the characteristic peak of O 1s at 530.2 eV may be assigned to Ti–O linkages [20,62]. The weak characteristic peak at 531.7 eV is closely related to –OH groups originating mainly from chemisorbed H_2O molecules [20,62].

In the N 1s spectrum, the characteristic peaks at 396–398 eV can be assigned to Ti–N–Ti structures [63]. Hence, the characteristic peak at 397.9 eV in Figure 3(e) should be attributed to the Ti–N–Ti structures generated upon the replacement of O atoms in the TiO_2 network [60]. According to previous studies, N 1s binding energy in a Ti–N–Ti environment is lower than that in N–Ti–O linkages [21]. Furthermore, the characteristic peaks of NO^- or NO_2^- species become visible above 400 eV [64] and hence the peak at 399.8 eV can be assigned to anionic N^- in N–Ti–O bonds. The characteristic peak at 401.5 eV can be ascribed to oxidized N atoms in Ti–O–N or Ti–O–N–O bonds; these N atoms are considered to be interstitial [65–67]. Additionally, the satellite peak at 407.1 eV originates from $\pi-\pi^*$ shake-up satellites due to the inclusion of π -electron structures (melamine residues) [68]. The relative atomic concentrations of N in MM-500, MM-600, and MM-700 were found to be 1.74, 1.22, and 1.01 atom%, respectively, indicating that the N-doping concentration decreased with an increase in calcination temperature. From these XPS results, it can be inferred that substitutional N was the dominating N-doping form embedded in TiO_2 lattices.

3.3. Electron microscopy

Fig. 3. XPS spectra of the as-prepared materials. (a) Survey, (b) C 1s, (c) Ti 2p, (d) O 1s, and (e) N 1s.

A scanning electron microscope (SEM), transmission electron microscope (TEM), and high-resolution transmission electron microscope (HRTEM) were used to evaluate the porous structure and surface morphology of the calcination products of MIL-125(Ti) and melamine mixtures. As illustrated in Figure 4(a), MIL-125(Ti) displayed a disk-like structure with a grain size of 500–600 nm, which is consistent with previous reports [46,47]. After pyrolysis, MM-500 basically retained the original shape of MIL-125(Ti) with a grain size of ~500 nm, suggesting that annealing did not affect the macro-structure (Figure 4(b)) of the photocatalyst. However, the disk-like structure of MM-500 can be visualized to consist of a number of crystalline grains 25–35 nm in diameter, which is consistent with the results of XRD analysis. The corresponding selected area electron diffractograms (SAED) are illustrated as an inset in Figure 4(c). A series of concentric rings in the SAED patterns suggests that the as-prepared N-TiO₂ crystals might orientate from amounts of directions. The corresponding spot-ring type SAED pattern can be indexed to anatase-rutile mixed structures. HRTEM images clearly show the sizes of the detected nanocrystals and lattice fringes of 0.351 and 0.324 nm (Figure 4(f)), which correspond exactly with the interplanar spacing of anatase TiO₂(101) and rutile TiO₂(110) planes [48,51], respectively.

3.4. N₂ adsorption-desorption

The N₂ adsorption-desorption isotherms and the corresponding Barrett-Joyner-Halenda (BJH) pore-size distribution curves of MM-500, MM-600, and MM-700 are shown in Figure 5. It can be observed that all the as-prepared photocatalysts exhibited type IV isotherms, which indicate mesoporous materials according to the IUPAC identification norms [21]. The

Brunauer-Emmett-Teller (BET) surface areas of MM-500, MM-600, and MM-700 were found to be 75.14, 25.19, and 13.48 m²·g⁻¹, respectively, suggesting that the BET surface areas of the fabricated N-TiO₂ decreased with an increase in calcination temperature. This phenomenon might be ascribed to the increase in crystalline grain size with an increase in calcination temperature; this observation is consistent with the results of XRD analysis. The pore volumes of MM-500, MM-600, and MM-700 were 0.294, 0.065, and 0.024 cm³·g⁻¹, respectively. Moreover, hysteresis loops in the range of ~0.7–1.0 P/P₀ further demonstrate the existence of mesopores inside MM-500, MM-600, and MM-700 [47,51]. MIL-125(Ti) possesses large pores (1.25 nm) and a high Ti content (24.5%, fully activated) [46] and hence, it is an ideal sacrificial precursor to construct porous TiO₂ at a relatively high yield. The mesopores are thought to be generated by the inter-aggregation of neighboring N-TiO₂ nanoparticles, as confirmed by SEM, TEM, and HRTEM analysis.

The relatively small crystalline grain size of the as-prepared N-TiO₂ can ensure a short path length for the migration of photo-induced carriers to reaction sites for photo-oxidation of the target contaminants. Meanwhile, their moderate BET surface areas imply that the as-prepared materials contain a large number reaction sites and transfer channels, which can facilitate the delivery and release of degradation products from reactant pollutants, thus comprehensively improving the photocatalytic reaction efficiency of the as-prepared disk-like N-TiO₂ [21,26,69]. In MIL-125(Ti), Ti(VI) atoms are coordinated with six O atoms to generate octahedron clusters and these octahedrons are connected by terephthalic acid bridges to form a 3D ordered network [44]. Therefore, the conversion from MIL-125(Ti) to N-TiO₂ as described in this study can effectively avoid long-range atomic migration [46], leading to a porous structure in MM-500, which is inherited from the porous MIL-125(Ti) template to a certain extent.

3.5. UV-visible diffuse reflection (UV-vis DRS) analysis

The UV-vis DRS patterns of MM-500, MM-600, MM-700, and the control material (P-25) are illustrated in Figure 6(a). In the case of MM-500, MM-600, and MM-700, a strong absorption intensity can be observed in the range of 400–800 nm; such absorption is missing in the spectrum of pristine TiO₂ (P-25). This phenomenon can be ascribed to the presence of N in MM-500, MM-600, and MM-700, which can strengthen the visible-light absorption efficiency of a material by narrowing its E_g [5]. Furthermore, the red-shift in the absorption spectra of MM-500, MM-600, and MM-700 is in accordance with a change in the material color from white (MM-700) to light yellow (MM-500), indicating that the level of N-doping is negatively correlated with calcination temperature.

As the prepared photocatalysts can be regarded as direct semiconductors, their E_g values were estimated using the Beer-Lambert equation (Equation (2)),

$$(ah\nu)^2 = A(h\nu - E_g) \quad (2)$$

where α is the absorption coefficient, A is a constant, and $h\nu$ is the photonic energy. Plots of $(ah\nu)^2$ versus $h\nu$ of the materials

Fig. 4. SEM images of (a) MIL-125 and (b) MM-500, (c) TEM and SAED images of MM-500, and (d)–(f) HRTEM images of MM-500.

Fig. 5. (a)–(c) N_2 adsorption-desorption isotherms and (d)–(f) BJH pore-size distribution curves of MM-500, MM-600, and MM-700.

Fig. 6. (a) UV-vis DRS and (b) $(\alpha h\nu)^2$ versus photo energy plots of MM-500, MM-600, MM-700, and P-25.

are shown in Figure 6(b). The E_g values of MM-500, MM-600, and MM-700 were estimated to be 2.87, 2.95, and 3.01 eV, respectively, which are considered suitable for the photodegradation of various types of organic contaminants under visible-light illumination. However, the E_g value of the control material was 3.13 eV, indicating that only UV light can be utilized for photodegradation reactions. Essentially, the bandgap narrowing should be ascribed to the contribution of N-doping as well as the O vacancies (O_v) incorporated in the TiO_2 lattice. This is because doped N atoms might generate new electronic states (substitutional or interstitial N) just above the valence band while O_v give rise to local states consisting of the 3d states of Ti^{3+} below the conduction-band edge [5,9,48,70]. In addition, previous studies also applied the density functional theory (DFT) to prove that N-doping is strongly inclined to induce the formation of O_v in bulk TiO_2 [9,71].

3.6. Photoluminescence (PL) and photoelectrochemical analysis

Considering that PL emission spectra are generated by the recombination of free photo-induced carriers, the separation efficiency of photo-induced electron and hole pairs can be measured by PL spectroscopy [72–74]. Figure 7(a) shows the PL spectra (425 nm excitation wavelength) of MM-500, MM-600, and MM-700. It can be observed that the PL intensity of MM-500 is higher than that of MM-600 and MM-700, which might be ascribed to the excitation of photo-induced electrons from the N- impurity level to the conduction band after N-doping. Later, the excited electrons were captured by O_v at the sub-band level. Finally, the photo-induced electrons captured by O_v recombined with the remaining h^+ at the N- impurity level to enhance the corresponding PL signal, as described by Equations (3) and (4).

The PL signals of the as-prepared photocatalysts were correlated with the N-doping content. Because the presence of N-

Fig. 7. (a) Photoluminescence spectra (excitation source: 425 nm), (b) ESR spectra, (c) Nyquist plots, and (d) photocurrent curves of MM-500, MM-600, and MM-700.

could induce the formation of O_v in the as-prepared photocatalysts, it can be concluded that the O_v content is related to the degree of N-doping. In other words, with an increase in calcination temperature, the N-doping and O_v content in the as-prepared photocatalysts reduced, thereby reducing the recombination probability of O_v and photo-induced electrons and finally reducing the corresponding PL intensities [75–77]. To validate this prediction, electron spin resonance (ESR) analysis was conducted to investigate the influence of calcination temperature on the formation of O_v in the as-prepared photocatalysts (Figure 7(b)). It can be clearly observed that ESR signals at the g -value (2.001) can be assigned to O_v in MM-500, MM-600, and MM-700 [78–80]. As expected, the O_v content gradually decreased with an increase in temperature, suggesting that the calcination temperature indeed affected the formation of O_v in the photocatalyst materials.

Additionally, the charge migration and recombination fate in the as-prepared photocatalysts were studied by photocurrent analysis and electrochemical impedance spectroscopy (EIS). Figure 7(c) shows the representative Nyquist plots of MM-500, MM-600, and MM-700. The semicircles in the EIS spectra can be attributed to charge-transfer resistance and a constant phase element at the photocatalyst/electrolyte interface [81,82]. It can be observed that the semicircle in the MM-500 spectrum had a larger radius than those of MM-600 and MM-700, suggesting that a high degree of N-doping accelerated photo-induced charge-carrier recombination, which is consistent with PL measurements. The photocurrent-time curves

of the as-prepared photocatalysts are displayed in Figure 7(d); the photocurrent intensities followed the order of MM-700 > MM-600 > MM-500, which indicates that MM-500 exhibited inferior charge migration and separation.

3.7. Photocatalytic activity toward gaseous benzene

The photocatalytic activities of MM-500, MM-600, MM-700, and P-25 were investigated in terms of the photodegradation of gaseous benzene under visible-light irradiation. Figure 8(a) displays the time-dependent photo-oxidation efficiencies of MM-500, MM-600, MM-700, and P-25 toward gaseous benzene after achieving adsorption-desorption equilibrium under dark conditions for 60 min. It can be clearly observed that gaseous benzene hardly degraded in visible light; the conversion efficiency of gaseous benzene was $\sim 15.4\%$ after 8 h of photolysis. Meanwhile, the removal efficiency was $\sim 13.9\%$ after 480 min without light irradiation. The photodegradation efficiency of P-25 was merely 50.9% under identical light illumination. However, in the case of MM-500, the photodegradation efficiency increased to 99.1% after N-doping. Furthermore, the mineralization of gaseous benzene was investigated with MM-500, MM-600, MM-700, and P-25. As shown in Figure 8(b), the amount of produced CO_2 was 302.4, 230.5, 124.4, and 70.2 ppmV corresponding to mineralization efficiencies of 72.0%, 54.9%, 29.6%, and 16.7% with MM-500, MM-600, MM-700, and P-25, respectively. The improved photocatalytic performance of MM-500 can be attributed to the enhanced absorption of

Fig. 8. (a) Photocatalytic degradation and (b) CO_2 produced during the photo-oxidation of benzene over MM-500, MM-600, MM-700, and P-25. (c) Cyclic experiments to evaluate the photostability and recyclability of MM-500 under visible-light illumination. (d) XRD patterns of MM-500 before and after benzene photodegradation experiments.

TiO_2 in the visible-light region after N-doping [10]. The $3d$ states of Ti^{3+} below the conduction band at ~ 1.2 eV are normally generated by trapping the electrons adjacent to O_v sites, which can contribute to visible-light absorption as color centers, thus dramatically increasing the photocatalytic activity [70]. Furthermore, because O_v is a significant active site to reduce chemisorbed O_2 to generate superoxide radicals ($\cdot O_2^-$) [9], it can be inferred that a large number of oxygen vacancies in MM-500 were responsible for the photo-oxidation of organic pollutants.

According to the previous studies, the Langmuir-Hinshelwood model can be selected to fit photocatalytic reactions using the following equation,

$$\ln(C_0/C) = kt \quad (5)$$

where C_0 is the initial concentration of gaseous benzene, C is the final concentration after t min of photodegradation, and t and k are the reaction time and corresponding first-order kinetic constant, respectively. From Figure S2, it can be observed that all the reactions fitted pseudo-first-order curves and their rate constants followed the order of MM-500 (0.01043 min^{-1}) > MM-600 (0.0053 min^{-1}) > MM-700 (0.00213 min^{-1}) > P-25 (0.00162 min^{-1}). This result further demonstrates that MM-500 exhibited the best photocatalytic performance under visible-light illumination. Furthermore, to assess the photochemical stability and recyclability of the as-prepared photocatalysts, cyclic photocatalytic degradation experiments on gaseous benzene were conducted using MM-500. As shown in Figure 8(c),

reused MM-500 did not display any apparent changes in its photocatalytic activity and it was estimated that 84.8% of benzene was photodegraded after 10 cyclic experiments. Moreover, the XRD pattern (Figure 8(d)) of the reused material was quite identical to that of the original MM-500, suggesting that MM-500 exhibits excellent photochemical stability.

3.8. Possible photodegradation mechanism

To better understand the photodegradation mechanism of gaseous benzene over the as-prepared materials, their valence states were confirmed by Mott-Schottky experiments (the Mott-Schottky curves of MM-600 and MM-700 are shown in Figure S2(a) and (b)). Consider MM-500 as an example (Figure 9); its flat-band potential (E_{FB}) was approximately -0.50 eV vs. Ag/AgCl. As for the n-type semiconductor, the E_{FB} is more positive (0.1 eV) than the conduction-band potential (E_{CB}) [83]. Hence the E_{CB} of MM-500 was -0.40 eV vs. NHE [73,74]. According to the E_g values obtained from UV-vis DRS spectra, the valence-band potential (E_{VB}) of MM-500 was estimated to be 2.47 eV.

The photodegradation process of gaseous benzene under visible-light irradiation is described in Figure 10(a). As described earlier, h^+ in the impurity level (interstitial and substitutional N) and photo-induced electrons in the conduction band are formed under visible-light irradiation (process A). Subsequently, free electrons might be energetically trapped by O_v

Fig. 9. Mott-Schottky curves of MM-500 at different frequencies.

(process B) and they may recombine with h^+ at N^- impurity levels to trigger PL (process C) [9,20,21]. In the case of TiO_2 -based photocatalysts, their capacity for the photo-oxidation of organic pollutants is mainly dependent on the available activated species, such as hydroxyl radicals ($\cdot OH$), $\cdot O_2^-$, and h^+ [84]. This is because the redox potentials of $OH^-/\cdot OH$ (+2.40 eV) [85] and $O_2/\cdot O_2^-$ (-0.33 eV) [86] are much lower than the E_{VB} (+2.47 eV) and E_{CB} (-0.40 eV) of MM-500, respectively. This allows the thermodynamic generation of $\cdot OH$ and $\cdot O_2^-$ via the oxidation of chemisorbed OH^-/H_2O and O_2 by photo-induced h^+ and e^- , respectively. Furthermore, benzene rings are commonly oxidized by $\cdot OH$ radicals and generate hydroxylated intermediates via hydroxylation [87]. The hydrox-

ylated intermediates are finally mineralized to CO_2 and H_2O . Meanwhile, $\cdot O_2^-$ can also react with gaseous benzene to mineralize it [88].

In addition, some direct oxidation processes might be triggered by h^+ in the valence band of the photocatalysts. According to previous studies, direct hole-attack reactions might form cation radicals, which hydrate gaseous benzene to generate hydroxylated compounds, such as phenol, 1,4-benzoquinone, and hydroquinone [89,90]. Reaction intermediates were not detected in our experiments because of the low initial concentration of gaseous benzene (~0.007%) and the relatively high photocatalytic efficiency of the as-prepared materials. Hence, the reactions shown in (10)–(14) are the only possible reaction pathways.

ESR analysis was conducted to examine the dominating O-containing active species involved in the photodegradation process. As illustrated in Figure 10(b) and (c), characteristic peaks of DMPO- $\cdot OH$ and DMPO- $\cdot O_2^-$ were detected in visible-light irradiated aqueous dispersions of MM-500, while no characteristic peaks corresponding to any radicals could be observed under dark conditions. The ESR results suggest that

Fig. 10. (a) Mechanism of the photocatalytic process on MM-500. (b) and (c) ESR spectra of $\cdot OH$ and $\cdot O_2^-$ active radicals trapped by DMPO on MM-500.

$\cdot\text{OH}$ and $\cdot\text{O}_2^-$ are the predominant species in the oxidation of gaseous benzene over MM-500.

4. Conclusions

In summary, a convenient and mild method was used to fabricate disk-like anatase-rutile mixed phase mesoporous N-TiO₂ via the calcination of MIL-125(Ti) and melamine mixtures in air. By varying the annealing temperature, different N-doping levels and phase structures were obtained in the photocatalysts. Because Ti–O structures in the as-prepared photocatalysts were generated from a porous MIL-125(Ti) template without long-range atomic migration, porosity is retained inside N-TiO₂. This synthesis method is beneficial for optical absorption and mass transfer during the photodegradation of gaseous benzene. The optimal photocatalyst (MM-500) exhibited enhanced photocatalytic performance when compared to commercial TiO₂. Photo-induced active radicals ($\cdot\text{OH}$ and $\cdot\text{O}_2^-$) were found to be the dominant species in the photodegradation of gaseous benzene. Furthermore, MM-500 exhibited excellent long-term cycling stability (the photocatalytic activity remained at 84.8% after 10 cyclic experiments), which indicates that MM-500 is a promising photocatalyst for the sustainable removal of different VOCs. More importantly, this study also demonstrates that MOFs are ideal precursors to prepare highly active porous metal-oxide photocatalysts.

References

- [1] Y. Hu, D. Li, Y. Zheng, W. Chen, Y. He, Y. Shao, X. Fu, G. Xiao, *Appl. Catal. B-Environ.*, **2011**, 104, 30–36.
- [2] J. Li, X. a. Dong, G. Zhang, W. Cui, W. Cen, Z. Wu, S. C. Lee, F. Dong, *J. Mater. Chem. A*, **2019**, 7, 3366–3374.
- [3] J. Li, W. Cui, P. Chen, X. a. Dong, Y. Chu, J. Sheng, Y. Zhang, Z. Wang, F. Dong, *Appl. Catal. B-Environ.*, **2020**, DOI: 10.1016/j.apcatb.2019.118130.
- [4] J. Ji, Y. Xu, H. Huang, M. He, S. Liu, G. Liu, R. Xie, Q. Feng, Y. Shu, Y. Zhan, R. Fang, X. Ye, D. Y. C. Leung, *Chem. Eng. J.*, **2017**, 327, 490–499.
- [5] Z. Shayegan, C.-S. Lee, F. Haghighat, *Chem. Eng. J.*, **2018**, 334, 2408–2439.
- [6] L. Zeng, Z. Lu, M. Li, J. Yang, W. Song, D. Zeng, C. Xie, *Appl. Catal. B-Environ.*, **2016**, 183, 308–316.
- [7] Y. Shu, J. Ji, Y. Xu, J. Deng, H. Huang, M. He, D. Y. C. Leung, M. Wu, S. Liu, S. Liu, G. Liu, R. Xie, Q. Feng, Y. Zhan, R. Fang, X. Ye, *Appl. Catal. B-Environ.*, **2018**, 220, 78–87.
- [8] S. Suárez, I. Jansson, B. Ohtani, B. Sánchez, *Catal. Today*, **2019**, 326, 2–7.
- [9] J. Wang, D. N. Tafen, J. P. Lewis, Z. Hong, A. Manivannan, M. Zhi, M. Li, N. Wu, *J. Am. Chem. Soc.*, **2009**, 131, 12290–12297.
- [10] G. Yang, Z. Jiang, H. Shi, T. Xiao, Z. Yan, *J. Mater. Chem.*, **2010**, 20, 5301–5309.
- [11] X. Liu, M. Ye, S. Zhang, G. Huang, C. Li, J. Yu, P. K. Wong, S. Liu, *J. Mater. Chem. A*, **2018**, 6, 24245–24255.
- [12] S. In, A. Orlov, R. Berg, F. García, S. Pedrosa-Jimenez, M. S. Tikhov, D. S. Wright, R. M. Lambert, *J. Am. Chem. Soc.*, **2007**, 129, 13790–13791.
- [13] S.-C. Moon, H. Mametsuka, S. Tabata, E. Suzuki, *Catal. Today*, **2000**, 58, 125–132.
- [14] T. Ohno, M. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui, M. Matsumura, *Appl. Catal. A-Gen.*, **2004**, 265, 115–121.
- [15] Y. Wang, J. Li, P. Peng, T. Lu, L. Wang, *Appl. Surf. Sci.*, **2008**, 254, 5276–5280.
- [16] Z. Lu, L. Zeng, W. Song, Z. Qin, D. Zeng, C. Xie, *Appl. Catal. B-Environ.*, **2017**, 202, 489–499.
- [17] X. Chen, C. Burda, *J. Am. Chem. Soc.*, **2008**, 130, 5018–5019.
- [18] G. Wu, J. Wang, D. F. Thomas, A. Chen, *Langmuir*, **2008**, 24, 3503–3509.

Graphical Abstract

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Robust photocatalytic benzene degradation using mesoporous disk-like N-TiO₂ derived from MIL-125(Ti)

Chen Zhao, Zhihua Wang *, Xi Chen, Hongyu Chu, Huifen Fu, Chong-Chen Wang *

Beijing University of Chemical Technology; Beijing University of Civil Engineering and Architecture

Mesoporous disk-like anatase-rutile mixed phase N-TiO₂ was constructed by the calcination of MIL-125(Ti) and melamine matrix in air, which possessed good photodegradation capability and superior cycling stability for photocatalytic purification of gaseous benzene.

- [19] C. Shifu, Y. Yunguang, L. Wei, *J. Hazard. Mater.*, **2011**, 186, 1560–1567.
- [20] F. Dong, W. Zhao, Z. Wu, S. Guo, *J. Hazard. Mater.*, **2009**, 162, 763–770.
- [21] D.-H. Wang, L. Jia, X.-L. Wu, L.-Q. Lu, A.-W. Xu, *Nanoscale*, **2012**, 4, 576–584.
- [22] X. Chen, D.-H. Kuo, D. Lu, *Chem. Eng. J.*, **2016**, 295, 192–200.
- [23] H. Irie, Y. Watanabe, K. Hashimoto, *J. Phys. Chem. B*, **2003**, 107, 5483–5486.
- [24] A. Petala, Z. Frontistis, M. Antonopoulou, I. Konstantinou, D. I. Kondarides, D. Mantzavinos, *Water Res.*, **2015**, 81, 157–166.
- [25] Z. Wu, F. Dong, W. Zhao, S. Guo, *J. Hazard. Mater.*, **2008**, 157, 57–63.
- [26] M. S. Akple, J. Low, Z. Qin, S. Wageh, A. A. Al-Ghamdi, J. Yu, S. Liu, *Chin. J. Catal.*, **2015**, 36, 2127–2134.
- [27] S. Yin, K. Ihara, M. Komatsu, Q. Zhang, F. Saito, T. Kyotani, T. Sato, *Solid State Commun.*, **2006**, 137, 132–137.
- [28] T. Sreethawong, S. Laehsatee, S. Chavadej, *Int. J. Hydrogen Energy*, **2008**, 33, 5947–5957.
- [29] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science*, **2001**, 293, 269–271.
- [30] J. Fang, F. Wang, K. Qian, H. Bao, Z. Jiang, W. Huang, *J. Phys. Chem. C*, **2008**, 112, 18150–18156.
- [31] D. Shingai, Y. Ide, W. Y. Sohn, K. Katayama, *Phys. Chem. Chem. Phys.*, **2018**, 20, 3484–3489.
- [32] H. Liu, Y. Ma, J. Chen, M. Wen, G. Li, T. An, *Appl. Catal. B-Environ.*, **2019**, 250, 337–346.
- [33] C.-C. Wang, X.-H. Yi, P. Wang, *Appl. Catal. B-Environ.*, **2019**, 247, 24–48.
- [34] C.-C. Wang, X.-D. Du, J. Li, X.-X. Guo, P. Wang, J. Zhang, *Appl. Catal. B-Environ.*, **2016**, 193, 198–216.
- [35] C.-C. Wang, J.-R. Li, X.-L. Lv, Y.-Q. Zhang, G. Guo, *Energy Environ. Sci.*, **2014**, 7, 2831–2867.
- [36] C. I. Ezugwu, S. Zhang, S. Li, S. Shi, C. Li, F. Verpoort, J. Yu, S. Liu, *Environ. Sci.-Nano*, **2019**, DOI: 10.1039/C9EN00871C.
- [37] Y. Kimitsuka, E. Hosono, S. Ueno, H. Zhou, S. Fujihara, *Inorg. Chem.*, **2013**, 52, 14028–14033.
- [38] X. Xiao, S. Peng, C. Wang, D. Cheng, N. Li, Y. Dong, Q. Li, D. Wei, P. Liu, Z. Xie, D. Qu, X. Li, *J. Electroanal. Chem.*, **2019**, 841, 94–100.
- [39] D. P. Dubal, K. Jayaramulu, J. Sunil, Š. Kment, P. Gomez-Romero, C. Narayana, R. Zbořil, R. A. Fischer, *Adv. Funct. Mater.*, **2019**, 29, 1900532–1900543.
- [40] S. Liu, J. Wang, J. Yu, *RSC Adv.*, **2016**, 6, 59998–60006.
- [41] H. Fu, X. Wang, P. Wang, Z. Wang, H. Ren, C.-C. Wang, *Dalton. T.*, **2018**, 47, 9014–9020.
- [42] X. Xu, R. Cao, S. Jeong, J. Cho, *Nano Lett.*, **2012**, 12, 4988–4991.
- [43] H. Niu, S. Liu, Y. Cai, F. Wu, X. Zhao, *Microporous. Mesoporous. Mat.*, **2016**, 219, 48–53.
- [44] M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez, G. Férey, *J. Am. Chem. Soc.*, **2009**, 131, 10857–10859.
- [45] J. Dou, Y. Li, F. Xie, X. Ding, M. Wei, *Cryst. Growth Des.*, **2016**, 16, 121–125.
- [46] Z. Wang, X. Li, H. Xu, Y. Yang, Y. Cui, H. Pan, Z. Wang, B. Chen, G. Qian, *J. Mater. Chem. A*, **2014**, 2, 12571–12575.
- [47] Z. Xiu, M. H. Alfaruqi, J. Gim, J. Song, S. Kim, T. V. Thi, P. T. Duong, J. P. Baboo, V. Mathew, J. Kim, *Chem. Commun.*, **2015**, 51, 12274–12277.
- [48] J. Li, X. Xu, X. Liu, W. Qin, L. Pan, *Cream. Int.*, **2017**, 43, 835–840.
- [49] J. Li, X. Liu, Z. Sun, L. Pan, *J. Colloid Interf. Sci.*, **2016**, 463, 145–153.
- [50] S. Hajiesmaili, S. Josset, D. Bégin, C. Pham-Huu, N. Keller, V. Keller, *Appl. Catal. A-Gen.*, **2010**, 382, 122–130.
- [51] Y. Gu, K. Cheng, Y.-N. Wu, Y. Wang, C. Morlay, F. Li, *ACS Sustain. Chem. Eng.*, **2016**, 4, 6744–6753.
- [52] M. Yan, F. Chen, J. Zhang, M. Anpo, *J. Phys. Chem. B*, **2005**, 109, 8673–8678.
- [53] D. Jiang, W. Wang, Y. Zheng, L. Zhang, *Appl. Catal. B-Environ.*, **2016**, 191, 86–93.
- [54] J.-H. Xu, W.-L. Dai, J. Li, Y. Cao, H. Li, H. He, K. Fan, *Catal. Commun.*, **2008**, 9, 146–152.
- [55] C. Ciardelli, I. Nova, E. Tronconi, D. Chatterjee, B. Bandl-Konrad, M. Weibel, B. Krutzsch, *Appl. Catal. B-Environ.*, **2007**, 70, 80–90.
- [56] A. M. Bernhard, D. Peitz, M. Elsener, A. Wokaun, O. Kröcher, *Appl. Catal. B-Environ.*, **2012**, 115–116, 129–137.
- [57] H. Li, J. Li, Y. Huo, *J. Phys. Chem. B*, **2006**, 110, 1559–1565.
- [58] S.-R. Zhu, P.-F. Liu, M.-K. Wu, W.-N. Zhao, G.-C. Li, K. Tao, F.-Y. Yi, L. Han, *Dalton. Trans.*, **2016**, 45, 17521–17529.
- [59] M. Yoshii, Y. Murata, Y. Nakabayashi, T. Ikeda, M. Fujishima, H. Tada, *J. Colloid Interface Sci.*, **2016**, 474, 34–40.
- [60] Y. Wei, M. Y. Li, X. J. Li, K. F. Yu, *New J. Chem.*, **2017**, 41, 8377–8381.
- [61] V. Etacheri, M. K. Seery, S. J. Hinder, S. C. Pillai, *Chem. Mater.*, **2010**, 22, 3843–3853.
- [62] O. Ruzimuradov, S. Nurmanov, M. Hojamberdiev, R. M. Prasad, A. Gurlo, J. Broetz, K. Nakanishi, R. Riedel, *J. Eur. Ceram. Soc.*, **2014**, 34, 809–816.
- [63] D. Mitoraj, H. Kisch, *Angew. Chem. Int. Ed.*, **2008**, 47, 9975–9978.
- [64] M. Sathish, B. Viswanathan, R. P. Viswanath, C. S. Gopinath, *Chem. Mater.*, **2005**, 17, 6349–6353.
- [65] G. Halasi, G. Schubert, F. Solymosi, *J. Catal.*, **2012**, 294, 199–206.
- [66] K. Zhang, X. Wang, X. Guo, T. He, Y. Feng, *J. Nanopart. Res.*, **2014**, 16, 2246.
- [67] Q. Xiang, J. Yu, W. Wang, M. Jaroniec, *Chem. Commun.*, **2011**, 47, 6906–6908.
- [68] K. Ichimura, Y. Nakahara, K. Kimura, H. Inokuchi, *J. Mater. Chem.*, **1992**, 2, 1185–1188.
- [69] O. Pikuda, C. Garlisi, G. Scandura, G. Palmisano, *J. Catal.*, **2017**, 346, 109–116.
- [70] S. Livraghi, M. C. Paganini, E. Giamello, A. Selloni, C. Di Valentin, G. Pacchioni, *J. Am. Chem. Soc.*, **2006**, 128, 15666–15671.
- [71] C. Di Valentin, G. Pacchioni, A. Selloni, S. Livraghi, E. Giamello, *J. Phys. Chem. B*, **2005**, 109, 11414–11419.
- [72] X.-H. Yi, F.-X. Wang, X.-D. Du, P. Wang, C.-C. Wang, *Appl. Organomet. Chem.*, **2019**, 33, 4621–4632.
- [73] X. Du, X. Yi, P. Wang, J. Deng, C.-C. Wang, *Chin. J. Catal.*, **2019**, 40, 70–79.
- [74] X.-D. Du, X.-H. Yi, P. Wang, W. Zheng, J. Deng, C.-C. Wang, *Chem. Eng. J.*, **2019**, 356, 393–399.
- [75] X. Pan, M.-Q. Yang, X. Fu, N. Zhang, Y.-J. Xu, *Nanoscale*, **2013**, 5, 3601–3614.
- [76] T. R. Gordon, M. Cargnello, T. Paik, F. Mangolini, R. T. Weber, P. Fornasiero, C. B. Murray, *J. Am. Chem. Soc.*, **2012**, 134, 6751–6761.
- [77] Y. Sun, H. Wang, Q. Xing, W. Cui, J. Li, S. Wu, L. Sun, *Chin. J. Catal.*, **2019**, 40, 647–655.
- [78] X. An, C. Hu, H. Liu, J. Qu, *J. Mater. Chem. A*, **2017**, 5, 24989–24994.
- [79] X. Xu, X. Ding, X. Yang, P. Wang, S. Li, Z. Lu, H. Chen, *J. Hazard. Mater.*, **2019**, 364, 691–699.
- [80] X. Li, W. Zhang, W. Cui, J. Li, Y. Sun, G. Jiang, H. Huang, Y. Zhang, F. Dong, *Chem. Eng. J.*, **2019**, 370, 1366–1375.
- [81] Y.-C. Zhou, X.-Y. Xu, P. Wang, H. F. Fu, C. Zhao, C.-C. Wang, *Chin. J. Catal.*, **2019**, 40, 1912–1923.
- [82] X.-H. Yi, S.-Q. Ma, X.-D. Du, C. Zhao, H. F. Fu, P. Wang, C.-C. Wang, *Chem. Eng. J.*, **2019**, 375, 121944–121957.
- [83] X. Jin, L. Ye, H. Wang, Y. Su, H. Xie, Z. Zhong, H. Zhang, *Appl. Catal. B-Environ.*, **2015**, 165, 668–675.
- [84] C. Ren, W. Qiu, H. Zhang, Z. He, Y. Chen, *J. Mol. Catal. A-Chem.*, **2015**,

- 398, 215–222.
- [85] X. Hu, W. Wang, G. Xie, H. Wang, X. Tan, Q. Jin, D. Zhou, Y. Zhao, *Chemosphere*, **2019**, 216, 733–741.
- [86] Y. Deng, L. Tang, G. Zeng, C. Feng, H. Dong, J. Wang, H. Feng, Y. Liu, Y. Zhou, Y. Pang, *Environ. Sci.-Nano*, **2017**, 4, 1494–1511.
- [87] Y. Li, B. Wen, W. Ma, C. Chen, J. Zhao, *Environ. Sci. Technol.*, **2012**, 46, 5093–5099.
- [88] T. D. Bui, A. Kimura, S. Higashida, S. Ikeda, M. Matsumura, *Appl. Catal. B-Environ.*, **2011**, 107, 119–127.
- [89] O. d'Hennezel, P. Pichat, D. F. Ollis, *J. Photochem. Photobiol. A*, **1998**, 118, 197–204.
- [90] J. Xu, Y. Ao, D. Fu, C. Yuan, *Appl. Surf. Sci.*, **2008**, 255, 2365–2369.

MIL-125(Ti)衍生介孔圆盘状N-TiO₂高效光催化降解气态苯

赵晨^{a,b}, 王志华^{a,*}, 陈 盼^b, 楚弘宇^b, 付会芬^b, 王崇臣^{b,#}

^a北京化工大学化工资源有效利用国家重点实验室, 北京100029

^b北京建筑大学建筑结构与环境修复功能材料北京重点实验室, 北京100044

摘要: 挥发性有机污染物(VOCs)对人或动物的危害较大, 具有致癌、致畸和致突变性。气固相光催化法已经成为一种具有广阔应用前景的VOCs治理技术。传统半导体光催化剂TiO₂带隙较宽($E_g = 3.2 \text{ eV}$), 太阳光利用效率低。特别是对光催化降解VOCs而言, 反应过程中产生的含碳类中间产物易在TiO₂表面积聚, 致使其失活。因此, 如何拓宽TiO₂的光谱响应范围, 提高量子效率及其在VOCs氧化过程中的循环利用性一直是研究重点。

由于O和N具有类似的化学结构和电子特征, 对TiO₂进行N掺杂(N-TiO₂)是实现TiO₂可见光催化的有效途径。TiO₂前驱体和氮源的种类对N-TiO₂的带隙、N掺杂位点、N掺杂量、形貌和孔径影响较大。金属-有机骨架(MOFs)具有结构多样且可调、多孔性、比表面积大等优点, 是制备特定形貌和结构的光催化材料的理想自牺牲模板。同时, 有机配体易于在高温煅烧过程中从MOFs骨架中释放, 其衍生物往往会继承MOFs的多孔性特征, 有利于光催化反应中间体的传输与释放。

本文采用MIL-125(Ti)作为前驱体, 三聚氰胺作为氮源, 通过在空气氛围下高温煅烧(温度分别为500, 600和700 °C)的方法制备了一系列具有可见光光催化活性的圆盘状介孔锐钛矿-金红石混合晶型的N-TiO₂ (分别标记为MM-500, MM-600和MM-700)。采用粉末X射线衍射(PXRD)、傅里叶变换红外光谱(FTIR)、扫描电子显微镜(SEM)、透射电子显微镜(TEM)、选区电子衍射(SAED)、X射线光电子能谱(XPS)、紫外-可见漫反射光谱(UV-vis DRS)和BET比表面积分析等对MM-500, MM-600和MM-700的形貌、组成及结构进行了表征。选取气态苯作为目标VOCs污染物探究了MM-500的光催化性能。

结果表明, 随着煅烧温度的提高, N掺杂含量减少, 所制备的光催化剂可见光吸收减弱, 锐钛矿相所占比例降低, N-TiO₂晶粒尺寸增大, 样品比表面积随之减少。由于MM-500优异的可见光吸收能力和传质能力, 其对气态苯表现出优异的光催化降解性能。可见光照射480 min后, MM-500对气态苯的去除效率高达99.1%, 矿化率达到72.0%, 均优于商业化二氧化钛(P-25)。循环实验表明MM-500具有较好的稳定性和重复利用性, 10次光催化实验后, 其对苯的去除效率仍达到84.8%。同时, 电子顺磁共振(ESR)证明超氧自由基($\cdot\text{O}_2^-$)与羟基自由基($\cdot\text{OH}$)是苯光催化氧化过程中的主要活性氧物种。综上, 本文以MIL-125(Ti)为前驱体所制备的N-TiO₂能高效光催化去除气态苯污染物。

关键词: 金属-有机骨架; N-二氧化钛; 可见光; 光催化氧化; 气态苯

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*通讯联系人. 电子信箱: zhwang@mail.buct.edu.cn

#通讯联系人. 电话/传真: (010)61209186; 电子信箱: chongchenwang@126.com, wangchongchen@bucea.edu.cn

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