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Article

Enhanced photocatalytic NO removal and toxic NO₂ production inhibition over ZIF-8-derived ZnO nanoparticles with controllable amount of oxygen vacancies

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ABSTRACT

The controlled introduction of oxygen vacancies (OVs) in photocatalysts has been demonstrated to be an efficient approach for improving the separation of photogenerated charge carriers, and thus, for enhancing the photocatalytic performance of photocatalysts. In this study, a two-step calcination method where ZIF-8 was used as the precursor was explored for the synthesis of ZIF-8-derived ZnO nanoparticles with gradient distribution of OVs. Electron paramagnetic resonance measurements indicated that the concentration of OVs in the samples depended on the temperature treatment process. Ultraviolet–visible spectra supported that the two-step calcined samples presented excellent light-harvesting ability in the ultraviolet-to-visible light range. Moreover, it was determined that the two-step calcined samples presented superior photocatalytic performance for the removal of NO, and inhibited the generation of NO₂. These properties could be attributed to the contribution of the OVs present in the two-step calcined samples to their photocatalytic performance. The electrons confined by the OVs could be transferred to O₂ to generate superoxide radicals, which could oxidize NO to the final product, nitrate. In particular, the NO removal efficiency of Z 350-400 (which was a sample first calcined at 350 °C for 2 h, then at 400 °C for 1 h) was 1.5 and 4.6 times higher than that of Z 400 (which was one-step directly calcined at 400 °C) and commercial ZnO, respectively. These findings suggested that OV-containing metal oxides that derived from metal-organic framework materials hold great promise as highly efficient photocatalysts for the removal of NO.

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1. Introduction

Nowadays, environmental problems and energy crises are causes of global concern. Nitric oxide (NO) is mainly produced

via the combustion of fossil fuels and automotive exhaust, and it is deemed to be a major contributor to the current atmospheric environmental problems. Moreover, trace amounts of NO could cause damage to the lungs, heart, liver, and kidneys,

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and therefore, NO is considered to be extremely harmful to human health [1–4]. Conventionally, various technologies and methods, such as selective adsorption, thermal catalysis, and selective catalytic reduction, have been widely used to eliminate the emission of gaseous NO [5–7]. However, traditional technologies aim to address high concentrations of NO generated from industrial sources under harsh conditions (high temperatures and pressures) instead of ppb levels of NO, which are present in the atmosphere. Recently, solar energy-based photocatalysis has been increasingly used for the effective removal of ppb levels of NO owing to the moderate reaction conditions, simple reaction processes, and high utilization of visible light [8–10].

ZnO, which is a promising semiconductor material, has been widely used for solar cells and photocatalysis owing to its favorable band edge positions, high catalytic efficiency, low cost, and environmental sustainability. However, the photocatalytic efficiency of ZnO is greatly hindered by its wide band gap, poor visible light absorption capacity, and rapid recombination of photogenerated electron-hole pairs. Many approaches, such as fabricating composite ZnO nanoparticles using different synthesis methods to dope metals, nonmetals, and noble metals, including simple hydrolysis, solvothermal treatment, and chemical deposition, have been developed to overcome these drawbacks [11–16]. In addition, previous reports have indicated that the introduction and regulation of oxygen vacancies (OVs) in the crystal lattice of ZnO could effectively enhance its photocatalytic efficiency owing to increasing its ultraviolet-visible (UV-Vis) light absorption and charge separation [17].

Recently, metal-organic frameworks (MOFs) have attracted significant attention for various applications, such as adsorption, photocatalysis, and thermal catalysis, owing to their properties, including their well-defined crystalline structure, high surface area, and large pore volume [18–23]. In particular, many efforts have been devoted to expanding the application of MOF materials for photocatalytic processes such as, the degradation of dyes [24], reduction of CO₂ [21,25,26], reduction of Cr (VI) [27], and production of H₂ [28]. ZIF-8, which is a zeolite imidazolate framework that consists of Zn²⁺ ions and imidazole or imidazole ligands, presents broad application prospects owing to its larger surface area, better chemical stability, and more facile synthesis method than those of other MOF materials, and consequently, it has been extensively explored for photocatalytic applications [29,30]. Owing to its large band gap of 5.1 eV, ZIF-8 can only absorb ultraviolet (UV) light, which limits the range of its applications under visible light irradiation. Consequently, most studies on ZIF-8 photocatalysts to date have focused on composite photocatalysts that comprised combinations of semiconductors and ZIF-8 or on ZIF-8-derived porous photocatalysts [31–33]. Nevertheless, a few studies on ZIF-8-derived ZnO photocatalysts with a certain concentration of OVs that have been used for the photocatalytic removal of low concentrations (ppb level) of NO have been reported.

In this study, we successfully synthesized ZnO nanoparticles with abundant OVs via a two-step calcination method using ZIF-8 as the precursor. The as-prepared samples, which contained OVs were used for the photocatalytic removal of NO

under visible light irradiation. The photocatalytic NO removal activity and capacity to inhibit the generation of NO₂ of the as-prepared samples were significantly higher than that of commercial ZnO (P-ZnO). Additionally, the possible promotion mechanism and NO removal process of the as-prepared samples have been carefully analyzed from various perspectives, including the amount of OVs (which was determined using electron paramagnetic resonance (EPR)), light absorption, and carrier recombination (which was analyzed using UV-Vis and photoluminescence (PL) spectra). The presence of OVs could significantly improve the absorption of visible light and separation of the photogenerated electron-hole pairs, and could also activate more O₂ to generate superoxide radicals ($\cdot\text{O}_2^-$), consequently, which accelerated the deep photocatalytic oxidation of NO. The strategy to fabricate OV-rich MOF-derived catalysts with excellent photocatalytic performance could be significant for expanding the use of MOF materials in the photocatalysis field.

2. Experimental

2.1. Chemicals

Zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O] was supplied by Tianjin KeMiou Chemical Reagent and 2-methylimidazole (2-MeIM), methanol, and ethanol were supplied by Aladdin. All materials and reagents were used as received, without further purification.

2.2. Photocatalyst synthesis

ZIF-8 nanocrystals were synthesized via a facile precipitation reaction method at room temperature, following procedures that have been previously reported in the literature [34]. Typically, Zn(CH₃COO)₂·2H₂O (2.19 g) and 2-MeIM (3.28 g) were dissolved in 100 and 25 mL methanol, respectively. Then, these solutions were mixed together under vigorous stirring, which was continued for 90 min. After the mixture was aged and reacted at room temperature for 24 h, the obtained solid was filtered, washed several times with ethanol, and was lastly dried overnight at 60 °C. The obtained sample was ZIF-8.

ZIF-8-derived ZnO nanoparticles were prepared via the calcination of the as-synthesized ZIF-8 powder in the muffle furnace using the two-step temperature method. Typically, a certain amount of ZIF-8 powder was placed in a porcelain boat and was heated to 350 °C for 2 h at the heating rate of 5 °C/min. Subsequently, individual samples were heated to 400, 450, and 500 °C for 1 h at the heating rate of 2 °C/min, and the obtained powders were collected and denoted as Z 350-400, Z 350-450, and Z 350-500, respectively.

For comparison, the same amount of ZIF-8 powder was directly calcined via one-step temperature processes at 400, 450, and 500 °C, respectively, for 3 h, at the heating rate of 5 °C/min, and the obtained powders were denoted as Z 400, Z 450, and Z 500, respectively.

2.3. Characterization

The X-ray diffraction (XRD) spectra of the samples were obtained using a D8 (Bruker) powder diffractometer with Cu $K\alpha$ radiation in the 2θ range of 20° – 80° . The morphology of the prepared samples was evaluated using a Verios 460 (FEI) field emission scanning electron microscopy (SEM) instrument, Tecnai G2 F20 S-TWIN (FEI) transmission electron microscopy (TEM) apparatus, and JEM-2100F (JEOL) high-resolution transmission electron microscopy (HRTEM) system. The X-ray photoelectron spectroscopy (XPS) profiles of the samples were obtained using an AXIS Supra (Kratos) instrument equipped with a monochromatic Ag $L\alpha$ X-ray source. The EPR signals of the prepared samples were obtained using a E500 (Bruker) EPR spectrometer. The PL spectra of the samples were recorded using a Lab RAM HR Evolution (Horiba) laser confocal Raman-transient fluorescence spectrometer with the excitation wavelength of 325 nm. The UV-Vis diffuse reflectance spectra (DRS) of the samples were obtained using a Cary 5000 (Agilent) ultraviolet-visible-near-infrared spectrophotometer over the wavelength range of 200–800 nm.

2.4. Photoelectrochemical measurements

The photoelectrochemical properties of the as-prepared samples were evaluated using an electrochemical workstation in a three-electrode quartz cells using saturated Na_2SO_4 solution as the electrolyte. The photocatalysts, Pt sheets, and Ag/AgCl electrodes were used as the working, counter, and reference electrodes, respectively. A 300 W Xe lamp was used as the light source and the working electrode was positioned 15 cm away from it.

2.5. Photocatalytic activity measurements

The photocatalytic performances of the prepared samples were evaluated for the photocatalytic oxidation of ppb levels of NO in a continuous-flow chamber under visible light irradiation. The capacity of the 30 cm $\times$ 15 cm $\times$ 10 cm flow reactor was 4.5 L. A 30 W LED lamp was vertically placed above the reactor and was used as the simulated visible light source. A mixture of NO and air was continuously flown through the reactor at the flow rate of 1 L/min, which was controlled using a mass flow controller, and came into contact with the surface of photocatalyst. The concentrations of NO and NO_2 were continuously recorded every minute using a 42i (Thermo Scientific) NO_x analyzer. Typically, 50 mg sample powder was dispersed in 10 mL water to form a homogeneous suspension, and then, the suspension was transferred into a disc-shaped dish ($R = 3$ cm). Subsequently, each sample was pretreated at 60°C to steam up the water, and was placed at the center of the reactor. After adsorption-desorption equilibrium (600 ppb) was reached, the LED lamp was turned on and the photocatalytic reaction began. The NO removal efficiency (η) was calculated using the following formula: $\eta = (1 - C/C_0) \times 100\%$, where C_0 and C are the inlet and outlet NO concentrations after adsorption-desorption equilibrium was reached, respectively. After the photocatalytic reaction was completed, the used photocatalysts were characterized using XRD, XPS, and TEM to evaluate their stability.

2.6. Trapping experiments

To elucidate the role of different active radicals during the photocatalytic reaction, active species radical capture experiments were carried out using potassium iodide (KI), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), tert-butyl alcohol (TBA) and p-benzoquinone (PBQ) as effective scavengers for the photo-generated holes (h^+), electrons (e^-), hydroxyl radicals ($\cdot\text{OH}$) and $\cdot\text{O}_2^-$ species, respectively [35]. Typically, 50 mg sample that contained different trapping agents were dispersed into 10 mL deionized water. Then, the suspensions were poured into glass dishes and dried at 60°C after 15 min of ultrasonic treatment. Lastly, the dishes were further used for NO removal experiments.

3. Results and discussion

3.1. Photocatalytic removal of NO

In this study, we evaluated the photocatalytic performance of different samples under visible light irradiation using an online NO_x analyzer for ppb-level NO removal. The photocatalytic experiments were carried out at room temperature in a continuous-flow reactor cylinder, and 0.05 g photocatalyst was used for the photocatalytic reaction. The lamp equipped with a 420 nm filter was turned on after the process reached adsorption-desorption equilibrium. ZIF-8 exhibited almost no NO photocatalytic removal performance under visible light irradiation, and that was attributed to its wide band gap and poor visible light absorption. All the ZIF-8-derived ZnO photocatalysts that were obtained using different temperature treatments exhibited enhanced photocatalytic NO removal efficiency compared to ZIF-8 and P-ZnO (Fig. 1(a)). The photocatalytic NO removal activity of Z 350-400 was much higher than those of Z 400, Z 450, Z 500, Z 350-450, and Z 350-500, and its NO_2 yield was relatively lower than those of the other photocatalysts (Fig. 1(b)). The NO removal ratio of Z 350-400 was approximately 36.7% (Fig. 1(c)) and was attributed to its preferable visible light absorption and numerous OV. In addition, Z 350-400 presented optimal photocatalytic degradation performance for TC (Fig. S1) under visible light irradiation. The XRD, XPS, and TEM characterization results of the used Z 350-400 (Figs. S2, S3, and S4, respectively) confirmed its excellent stability.

3.2. Structure, morphology, and OVs of photocatalysts

XRD analysis was used to determine the crystal structures of the as-prepared samples. Fig. 2 presents the XRD patterns of the samples obtained at different calcination temperatures. Some ZnO-characteristic peaks were observed in the XRD profiles of the ZIF-8-derived ZnO samples, where the distinct diffraction peaks (2θ) of 32.1° , 34.4° , 36.5° , 47.7° , 57.1° , 63.1° , 67.0° , and 68.4° could be attributed to the (100), (002), (101), (102), (110), (103), (200), and (112) crystal planes of ZnO (JCDPS No. 75-1526), respectively. In addition, all the observed XRD peaks were sharp and strong, which indicated that the

Fig. 1. (a) Photocatalytic performance of different photocatalyst samples for removal of NO under visible light irradiation; (b) corresponding amount of NO₂ generated over different photocatalyst samples; (c) NO removal performance of different photocatalyst samples.

ZIF-8-derived ZnO samples presented good crystallinity and high purity. Moreover, the intensities of the characteristic peaks increased as the calcination temperature of the samples was higher, that is: Z 350-400 < Z 350-450 < Z 350-500 and Z 400 < Z 450 < Z 500, which suggested that the particle size and crystallinity of ZnO increased in the same order.

The morphologies and structures of ZIF-8, Z 400, and Z 350-400 were characterized using SEM and TEM (Fig. 3). The SEM and TEM images in Figs. 3(a) and (d), respectively, revealed that the as-prepared ZIF-8 sample consisted of cubic particles with smooth surface, which was in agreement with the information previously reported in the literature [36]. When ZIF-8 was directly calcined at 400 °C, the obtained Z 400 sample consisted of distorted rhombic dodecahedral particles (Fig. 3(b)) and the ZnO nanoparticles formed large aggregates (Fig. 3(e)). The above phenomena illustrated that the one-step calcination method could remove the organic groups from the structure of ZIF-8 but caused its structure to collapse easily and facilitated the polymerization of the ZnO particles. Therefore, controlling the calcination conditions is very important for producing small and uniform ZnO particles that are free of organic groups and no longer present organic framework structure. In this study, a two-step calcination method has been used to prepare uniform ZnO samples. As illustrated in Fig. 3(c), the two-step calcination method could generate ZnO particles that featured the rhombic dodecahedral morphology of the ZIF-8 frames, which indicated that the first treatment step (at 350 °C) could partially remove the organic groups, whereas the second treatment step (at 400 °C) could remove the excess organics,

and thus increase the crystallization of ZnO. Moreover, the Z 350-400 sample retained its polyhedral microtopography, and the ZnO nanoparticles located on its surface (Fig. 3(f)) appeared to be smaller than those on the surface of Z 400 (Fig. 3(e)). This could have been caused by the heating rate of Z 400 being higher than that of Z 350-400. Rapid increase in temperature more likely caused structural damage and the agglomeration of ZnO particles.

To further confirm the coexistence of ZnO, the HRTEM images of prepared samples were obtained and the results are displayed in Figs. 4(a) and (b). The HRTEM images of Z 350-400 and Z 400 exhibit distinct lattice fringes, which indicated the good crystallinity of the samples. The lattice fringes of 0.278 and 0.274 nm corresponded to the (100) plane of ZnO, which further confirmed the presence of ZnO in the samples.

To investigate their chemical composition and elemental state, we subjected the Z 400 and Z 350-400 samples to XPS analysis. The survey scan XPS profile (Fig. 5(a)) revealed that the Z 400 and Z 350-400 samples consisted mostly of Zn, O, and C; furthermore, the N content of both samples was beyond the detection limit. The O and Zn contents of Z 350-400 were 36.77 and 11.20 at%, respectively, which were higher than those of Z 400: 23.72 and 3.01 at%, respectively (Table S1). Moreover, the O 1s XPS profiles of ZnO are illustrated in Fig. 5(b). The three peaks centered at approximately 529.9, 531.5 and 533 eV in the high resolution O 1s XPS spectra of the Z 350-400 and Z 400 samples could be ascribed to the lattice O²⁻ ions of ZnO, OVs, and adsorbed oxygen (H₂O), respectively [17]. The peak value percentages of Z 350-400 and Z 400 were 54.4% and 41.6%, respectively, which indicated that Z 350-400 contained a higher

Fig. 2. XRD patterns of different samples.

Fig. 3. SEM (a–c) and TEM (d–f) images of ZIF-8 (a, d), Z 400 (b, e) and Z 350-400 (c, f).

Fig. 4. HRTEM images of Z 350-400 (a) and Z 400 (b).

amount of surface OV than Z 400. Thus, the XPS results suggested that the ZIF-8-derived ZnO samples presented different concentrations of OV, which depended on the calcination temperature; moreover, Z 350-400 contained more OV than Z 400, which was good agreement with the EPR results. The Zn 2p XPS profiles of the two samples are presented in Fig. 5(c). The two characteristic peaks of Zn at 1044.5 and 1021.5 eV in the high-resolution XPS profile corresponded to Zn 2p_{1/2} and Zn 2p_{3/2}, respectively. The distance between the two lines was determined to be 23.0 eV, which suggested that both samples contained Zn²⁺ ions, according to the spectra reported in the literature [37]. The Zn 2p_{1/2} and Zn 2p_{3/2} peaks in the high-resolution Zn 2p XPS profile of Z 350-400 (Fig. 5(c)) shifted toward lower binding energies compared to those of Z 400. Moreover, the peaks in the O 1s XPS profile of Z 350-400 shifted toward lower binding energies compared to those of Z 400 (Fig. 5(b)). The shifting of Zn 2p and O 1s peaks should be ascribed to the presence of OV in these samples, which facilitated the enrichment of electrons and transfer of electrons to the Zn and O atoms of the Z 350-400 sample [38].

EPR is typically considered to be a sensitive technique for the detection of OV that feature unpaired electrons in photocatalysts. Significant signal peaks at $g = 2.001 \pm 0.002$ were observed for all ZIF-8-derived ZnO samples, and were attributed to the presence of surface OV [39, 40]; moreover, the intensity of the signal decreased as the calcination temperature increased as follows: Z 350-400 > Z 350-450 > Z 350-500 (Fig. 6). These results illustrated that the ZIF-8-derived ZnO with gradient distribution of OV had been successfully synthesized via the facile two-step calcination method. Furthermore, the signal intensities of the two-step calcined samples were stronger than those of the one-step directly calcined samples, which indicated that the two-step calcination method was

Fig. 6. EPR signals of analyzed photocatalysts.

more beneficial for the formation of OV on the surface of ZnO. Thus, it was beneficial to produce active species such as $\cdot\text{O}_2^-$ or $\cdot\text{OH}$ to enhance the performance of the photocatalysts.

Furthermore, the PL spectra of P-ZnO, Z 400, and Z 350-400 were recorded to explore the behavior of their photogenerated charge carriers. All three samples exhibited UV emission at approximately 380 nm, which should be ascribed to the intrinsic band-to-band emission, and corresponded to the recombination of the surface electron-hole pairs (Fig. 7). In addition, the Z 350-400 sample presented a new broad peak band at 530–550 nm, which was attributed to the defect-related emission [41]. P-ZnO presented higher PL intensity at 380 nm than the other samples, and that was attributed to the recombination of a certain amount of photogenerated electron-hole pairs. Moreover, the signal intensity of Z 350-400 was the weakest, which indicated that the recombination rate of photogenerated carriers was largely suppressed for this sample. The above results suggested that a significant amount of OV had been successfully introduced into the prepared ZnO particles and particularly at their surface [42]. The proposed surface OV could act as electron traps for the photogenerated electrons and could increase the opportunity of electron transitions from the OV energy level to the valence band.

To further investigate the roles of OV during the photocatalytic removal of NO, the optical absorption properties and energy band gaps of the photocatalyst samples were studied using UV-Vis DRS data. Compared to P-ZnO and ZIF-8, all ZIF-8-derived ZnO samples exhibited an extra absorption peak in the visible light region which could be attributed to the generated OV (Fig. 8(a)). In addition, the Z 350-400 sample exhib-

Fig. 5. XPS profiles of Z 400 and Z 350-400. (a) Full scan; (b) O 1s; (c) Zn 2p.

Fig. 7. PL spectra of P-ZnO, Z 400, and Z 350-400.

ited preferable visible light absorption, unlike the other samples. According to the literature [17], substances that form OV's owing to the loss of O atoms will form a color center, resulting in the color change. Therefore, it was concluded that the formation of surface OV's was beneficial for improving the light absorption properties of photocatalysts.

The band gap energies of the photocatalysts in this study were calculated using the Kubelka-Munk formula: $\alpha h\nu = A(h\nu - E_g)^{1/2}$, where α , h , ν , A , and E_g are the absorption coefficient, the Planck constant, the frequency of light, a constant, and the absorption band gap energy, respectively [43–45]. The value of η depends on the optical transition type of the semiconductor photocatalyst, and $\eta = 1$ for the systems in our study because ZnO is a direct band gap semiconductor [46]. The approximate band gaps of P-ZnO, Z 400, Z 450, Z 500, Z 350-400, Z 350-450, and Z 350-500 were 3.22, 3.15, 3.18, 3.19, 3.10, 3.14, and 3.17 eV, respectively (Fig. 8(b)). The band gap decreased as the concentration of OV's increased, and that could be attributed to the upshift in the valence band maximum and downshift in the conduction band minimum, which reduced the redox capacity of the photogenerated electrons and holes. However, the prepared samples still possessed suitable band gaps which were attributed to the appropriate calcination treatment; moreover, the introduction of OV's could improve the photocatalytic NO removal efficiency of the prepared samples.

Moreover, the increased visible light absorption ability of the photocatalysts could improve their performance by increasing their photon-absorption capacity, generating more charge carriers, and enhancing their photocatalytic NO removal efficiency (Fig. 1).

3.3. Photoelectrochemical performance

To further appraise the separation efficiency of the photo-generated electron-hole pairs, transient photoelectrochemical experiments were performed, and the results are illustrated in Fig. 9. The photocurrent density of Z 350-400 was significantly higher than those of Z 400 and P-ZnO under the experimental conditions in this study, during six on-off cycles (Fig. 9(a)), which indicated that Z 350-400 presented lower photogenerated electron-hole recombination rate and higher electron transport than Z 400 and P-ZnO. These results were in agreement with the DRS and PL results. In addition, electrochemical impedance spectrum experiments were performed to investigate the electron transfer behaviors of the samples. The Nyquist plot radius of Z 350-400 was smaller than those of Z 400 and P-ZnO, which revealed that Z 350-400 exhibited better separation of its electron-hole pairs and more photogenerated charge carriers than Z 400 and P-ZnO, and, consequently, it presented higher photocatalytic NO removal performance.

3.4. Possible photocatalytic oxidation mechanism

The proposed photocatalytic removal mechanism of NO over Z 350-400 is depicted in Fig. 10. On one hand, the enhanced NO oxidation effect was mainly attributed to the presence of OV's in Z 350-400. The OV's could efficiently promote the separation of the photogenerated electron-hole pairs [47–51], and the photogenerated electrons could easily migrate toward the OV's on the sample surface, where they could be immediately trapped. Then, the trapped electrons and oxygen on the sample surface could produce $\cdot O_2^-$ species, which could more easily facilitate the photocatalytic transformation of NO into nitrate, the final reaction product ($NO + \cdot O_2^- \rightarrow NO_3^-$). Conversely, the restructured holes could accumulate in the valence

Fig. 8. UV-vis DRS spectra (a) and energy band gaps (E_g) (b) of samples.

Fig. 9. Photocurrent responses under Xe lamp irradiation (a) and EIS (b) measurements of ZIF-8, P-ZnO, Z 400, and Z 350-400.

band of the sample and oxidize H_2O to $\cdot\text{OH}$. Thus, NO could be effectively oxidized to $\text{NO}_2/\text{NO}_3^-$ by the generated $\cdot\text{OH}$.

To further elucidate the photocatalytic removal mechanism of NO over Z 350-400, a series of trapping experiments were performed. Compared to the photocatalytic removal of NO in the absence of trapping agents, the NO removal efficiency was significantly reduced after the addition of KI and $\text{K}_2\text{Cr}_2\text{O}_7$ to the reaction mixture (Fig. 11), which suggested that the photogenerated holes and electrons were both efficient for the removal of NO. In addition, the NO removal efficiency decreased after PBQ was added to the reaction mixture, which indicated that

Fig. 10. Possible photocatalytic removal mechanism of NO over Z 350-400.

Fig. 11. Trapping experiments using Z 350-400.

the $\cdot\text{O}_2^-$ species played an important role during the NO removal

process. The addition of TBA to the reaction mixture could also inhibit the removal of NO; but yet have some photocatalytic efficiency, which implied that $\cdot\text{OH}$ played a secondary role in this reaction system compared to $\cdot\text{O}_2^-$.

Therefore, the presence of OV in Z 350-400 significantly promoted the transfer of photogenerated charges and boosted the generation of $\cdot\text{O}_2^-$ species, which could accelerate the deep photocatalytic oxidation of NO. In brief, Z 350-400 presented excellent light-harvesting ability in the UV to visible light wavelength range, which significantly enhanced the generation of more active photoelectrons and holes on its surface. More importantly, the abundant OV formed in this photocatalyst could represent active adsorption and reaction sites, and could improve the activity of the photocatalysts in addition to producing a sufficient number of electrons. The increased adsorption capacity also contributed to the improved NO photo-oxidation efficiency. The following possible removal mechanism of NO over Z 350-400 was proposed:

4. Conclusions

In summary, ZnO nanoparticles with OV have been successfully prepared via a facile two-step calcination method using ZIF-8 as the precursor. Compared to the one-step directly calcined samples and P-ZnO, the two-step calcined samples presented significantly higher performance for the photocatalytic removal of NO and for inhibiting the generation of NO_2 owing to the presence of generated OV, which were beneficial for the separation and transfer of the photogenerated electron-hole pairs and absorption of light. Furthermore, the formed OV could easily trap and confine photogenerated electrons to activate O_2 and produce more $\cdot\text{O}_2^-$ species, and thus, improved the NO oxidation ability and photocatalytic efficiency

of the as prepared samples. This study could provide a strategy toward the design of highly efficient photocatalysts for the removal of NO using MOFs as promising precursors.

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Graphical Abstract

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Enhanced photocatalytic NO removal and toxic NO₂ production inhibition over ZIF-8-derived ZnO nanoparticles with controllable amount of oxygen vacancies

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ZIF-8 was used as precursor for two-step calcination synthesis of ZnO nanoparticles with controlled OV, which were used to effectively remove NO under visible light irradiation.

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ZIF-8衍生的具有可控氧空位的ZnO对光催化去除NO的增强及毒性NO₂形成的抑制

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摘要: 氧化锌作为一种半导体材料, 具有合适的能带结构位置, 高催化效率, 低成本和环境可持续性, 因而广泛用于光催化领域。然而, 由于氧化锌的宽带隙, 可见光吸收能力差以及光生电子-空穴对的快速复合, 极大地影响了其光催化效率。通过引入氧空位调控光催化剂的结构被证明是一种可以改善光生载流子的分离, 从而提高光催化性能的有效方法。

本文以ZIF-8为前驱体, 采用两步煅烧法合成了具有不同浓度氧空位分布的ZnO纳米光催化剂, 通过X射线衍射(XRD)、扫描电镜(SEM)、透射电镜(TEM)、紫外-可见漫反射光谱(UV-Vis DRS)、X射线光电子能谱(XPS)、电子顺磁共振(EPR)、荧光光谱仪(PL)等手段系统地分析了合成的光催化剂的理化性质, 并评价了它们在可见光下光催化氧化去除NO反应性能。

EPR结果表明, 样品中氧空位的浓度取决于温度处理的过程。通过两步煅烧法得到氧化锌中氧空位的含量高于一步直接煅烧法所得的样品。此外, 随着煅烧温度升高, 合成的氧化锌晶格越完好, 其氧空位含量越少。UV-Vis DRS结果表明, 两步煅烧法合成的ZnO与商业的ZnO及一步法直接煅烧合成的ZnO相比, 其吸光范围从紫外光拓展到了可见光, 表现出了更加优异的吸光性能。光催化反应结果表明, 与商业氧化锌和一步直接煅烧法所得样品相比, 两步煅烧法合成的样品表现出了更优异的光催化去除NO性能, 并抑制了中间产物毒性NO₂的产生, 促进了NO的深度氧化。具体反应路径为: 在光照过程中, 光生电子很容易被氧空位俘获, 与O₂反应产生更多的超氧自由基(·O₂⁻), 从而将NO氧化成最终的产物硝酸盐。尤其有趣的是, 先在350 °C煅烧2小时再400 °C煅烧1小时的两步法样品Z 350-400的NO去除效率分别比一步法样品Z 400(400 °C煅烧)和商用ZnO高出1.5和4.6倍。这表明以MOF材料衍生的具有适当量氧空位的金属氧化物为一种高效去除NO的光催化剂具有很好的应用前景。

关键词: 光催化去除NO; ZIF-8; 氧化锌; 氧空位; 温度处理

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