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Article

C_3N_4 modified with single layer ZIF67 nanoparticles for efficient photocatalytic degradation of organic pollutants under visible light

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ABSTRACT

Uniformly distributed single layer of ZIF67-derived C_3N_4 (ZIF67- C_3N_4) was synthesized and applied to the photocatalytic degradation of methylene blue (MB) under visible light. Results indicated that the obtained ZIF67- C_3N_4 has a maximum specific surface area of 541.392 m²/g, which is much larger than that of raw C_3N_4 of 97.291 m²/g. The investigation of C_3N_4 amount involved in ZIF67- C_3N_4 on the photoactivity revealed that 2.57 g ZIF67 with 0.3 g C_3N_4 , which named ZIF67- C_3N_4 (0.3) exhibited superior photocatalytic activities. More than 90% of MB at 10 mg/L was degraded within 70 min with the addition of 0.01 g ZIF67- C_3N_4 (0.3), while this time required for raw C_3N_4 was over 140 min. The effects of pH of solution, initial concentration of MB and dosage of C_3N_4 in ZIF67- C_3N_4 composites on the photocatalytic efficiency for MB degradation were also evaluated. Quenching experiments indicated that the photo-induced holes (h^+) and superoxide radicals ($O_2^{\cdot-}$) were mainly responsible for MB degradation. It is anticipated that the insertion of ZIF67 nanoparticles not only increases the adsorption capacity of C_3N_4 but also promotes the generation and migration of the photo-induced active species.

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1. Introduction

With the ever-increasing in the organic industry globally, water pollution caused by organic contaminants has been a worrisome problem due to most of the organics are persistent and difficult to degrade in the environment. To date, adsorption and photocatalysis decomposition are considered to be two of the most promising methods for removing organic pollutants in aqueous solutions [1,2]. The past years have witnessed the

dramatic development of photocatalysis on account of its economic, recyclable, sustainable and high efficiency. As one of the most favored technologies, visible light enhanced photocatalysis has been widely studied in the treatment of organic contaminants and destructive substances in water due to its energy-conservation and clean peculiarities [3–5]. Semiconductor photocatalysts, such as TiO_2 [6–8], ZnO and $ZnFe_2O_4$ [9,10], and C_3N_4 [11–13] were widely used in visible light-driven photocatalysis processes.

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Among the above-mentioned photocatalysts, C_3N_4 with a bandgap of 2.7 eV has drawn increasing attention for its application in photocatalysis as well as photochemical hydrogen production because of its cost-efficient, visible light response, environmental sound, chemical and photocatalytic stability [11,14,15]. However, the main imperfections of the C_3N_4 are that it suffers from the high recombination with photoexcited charge carriers and low specific surface area. To reduce the probability of recombination with other charge carriers, efforts have put on the coupling of C_3N_4 with other suitable semiconductors. For instance, $ZnO-C_3N_4$ [16,17], $TiO_2-C_3N_4$ [18,19], $Bi_2WO_6-C_3N_4$ [20–22], $BiVO_4-C_3N_4$ [23–25] were developed to alleviate the recombination probability of C_3N_4 and improve the photocatalytic activities against organic pollutants. However, there is still a lack of research on the restrictions caused by the low surface area of C_3N_4 .

In recent years, metal-organic-frameworks (MOFs) that consist of metal ions and organic ligands emerged and proved to be preeminent templates with super large surface area and excellent porous structure. MOFs have attracted great interest in various applications such as energy storage, separation, and catalysis [26–30]. To date, MOFs have already been employed in the reduction of CO_2 [31,32] and O_2 [33], and the electrocatalytic evolution of H_2 [34] in the past few years. Besides, some of the MOFs themselves could participate in the photocatalysis [35,36]. Hence, developing valuable manners to introduce photocatalytic MOFs into C_3N_4 is of great economic benefit.

In the present study, a foundational Co-based MOF material, zeolitic imidazole framework (ZIF)-ZIF67 nanoparticles were introduced into C_3N_4 through a facile synthesis process at room temperature. The microstructure and morphology analysis revealed that the synthesis process developed in this work has no damage on the photocatalytic properties for C_3N_4 itself. The harvest ZIF67-based C_3N_4 , ZIF67- C_3N_4 hereafter, was used for photocatalytic degradation of methylene blue (MB) in aqueous solutions under various conditions. The effect of influencing factors such as pH of the solution, initial concentration of pollutants and amount of C_3N_4 on the photocatalytic efficiency for MB degradation were also evaluated.

2. Experimental

2.1. Materials and chemicals

Methylene blue trihydrate ($C_{16}H_{18}ClN_3S \cdot 3H_2O$, 99.5%), and ammonium chloride (NH_4Cl , 99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. $Co(NO_3)_2 \cdot 6H_2O$ (99%), 2-methylimidazole ($C_4H_6N_2$, 98%) were purchased from Shanghai Macklin Biochemical Co., Ltd. Methanol (CH_4O , HPLC grade, 99.9%) was obtained from Fisher Scientific. Ethanol absolute (CH_3CH_2OH , 99.7%) was supported by Beijing Chemicals Works. Dicyandiamide ($C_2H_4N_4$, 99%) was purchased from Energy Chemicals, Shanghai. Milli-Q water ($\rho = 18.2 M\Omega \cdot cm$) produced from a Milli-Q purification system (Millipore, Billerica, MA) was used to prepare MB solutions. All the chemicals in this study were used as received without any purification.

2.2. Synthesis of C_3N_4

In this study, the C_3N_4 was prepared by mixing of 2.0 g $C_2H_4N_4$ with 10.0 g NH_4Cl in a crucible. After grinding thoroughly, the crucible was placed in a Muffle furnace. The temperature was then heated to 550 °C at a rate of 3 °C/min and kept at 550 °C for 4 h. After cooling down to room temperature, the harvested C_3N_4 was ground and stored in a sealed plastic bag.

2.3. Synthesis of ZIF67- C_3N_4 catalyst

To synthesize ZIF67- C_3N_4 , 0.58 g of $Co(NO_3)_2 \cdot H_2O$ was added into 30 mL of methanol and stirred thoroughly as solution #1, and 0.99 g of 2-methylimidazole was dissolved into 10 mL of methanol as solution #2. The solution #2 was then poured into solution #1 slowly along with stirring to make the homogeneous solution. The designed amount of prepared C_3N_4 (g) was gradually added into the above solution and the mixture was placed on a magnetic stirrer and stirred for a period of 24 h at 400 rpm. The resulted ZIF67- C_3N_4 precursor was then centrifuged at 8000 rpm for 5 min followed by rinsing using ethanol for at least 3 times. After drying in a vacuum oven overnight at 65 °C the final ZIF67- C_3N_4 was obtained. Five different ZIF67- C_3N_4 composites were synthesized based on the loading amount of C_3N_4 , named ZIF67- C_3N_4 (0.1), ZIF67- C_3N_4 (0.2), ZIF67- C_3N_4 (0.3), ZIF67- C_3N_4 (0.4), and ZIF67- C_3N_4 (0.5). The numbers in the suffix parentheses represent the dosage of C_3N_4 in ZIF67- C_3N_4 composites.

2.4. Materials characterization

The crystal structures of the synthesized samples were identified using X-ray diffraction (XRD, X' Pert Pro), the 2-theta ranging from 10° to 90° by a step width of 0.033° with 15.24°/min speed at 40 mA and 40 kV. The morphology of the samples was analyzed by scanning electron microscopy (SEM) (SU8020, Hitachi) and transmission electron microscope (TEM) (HT7700, Hitachi). The chemical bonding of the samples was identified using Fourier transform infrared (FT-IR) spectrometer (Nicolet 8700, Thermal Fisher Scientific). X-ray photoelectron spectroscopy (XPS) analyses were acquired using ESCALAB250Xi spectrometer in the range of 4000–500 cm^{-1} . The specific surface area and pore size distribution of the samples were examined using Brunauer-Emmett-Teller (BET) theory based on the N_2 adsorption and desorption isotherms on an AUTOSORB-1 surface area and pore size analyzer (Quantachrome Instruments). The UV-vis diffuse reflectance spectrum (DRS) of C_3N_4 , ZIF67, and ZIF67- C_3N_4 composite was recorded using a spectrophotometer (Hitachi 3010, Japan).

2.5. Adsorption test

In order to evaluate the effect of adsorption on the photocatalytic test in this study, the adsorption performances of the synthesized C_3N_4 , ZIF67, and ZIF67- C_3N_4 were examined through a series of adsorption test. For single adsorption, an

aliquot of 0.01 g sample was added in 100 mL of designed concentrations of MB solutions. The mixtures were then placed in the dark environment with stirring at 200 rpm for a period of 180 min. To collect the absorbance of the processed liquid for a set period of time, a total volume of 3 mL of the MB solution was taken out using a syringe and filtered through 0.45 μm filter for UV-vis analysis (UV-Vis 2600, Shimadzu). The adsorption behavior of MB by the catalysts was then evaluated based on the variation in the absorbance of the MB solutions.

2.6. Photocatalytic ability of the catalysts

The photocatalytic performance of C_3N_4 , ZIF67, and ZIF67- C_3N_4 was evaluated through degradation of MB under visible light. Generally, an aliquot of 0.01 g catalyst was added to 100 mL of different concentrations of the MB solutions in a 6 cm $\times$ 5 cm $\times$ 5 cm (height $\times$ length $\times$ width) quartz glass reactor. The initial concentrations of MB were set to be 5, 10, 15, and 20 mg/L, respectively. The reactor was then stirred at 200 rpm under PLS-SXE300 Xenon lamp irradiation with a 420 nm cut-off filter, the distance between light to the surface of the liquid was about 8 cm. The photocatalytic test was quitted at 140 min based on a pre-test. Both of the adsorption and photocatalytic degradation performance of MB by different catalysts were described according to the following equation:

$$R = (1 - C/C_0) \times 100\% \quad (1)$$

Where R stands for the removal efficiency of MB (%), C and C_0 represent the concentrations of MB at different reaction times and the initial concentrations of MB (mg/L), respectively.

3. Results and discussion

3.1. Material characterization

The XRD patterns of synthesized C_3N_4 , ZIF67, and ZIF67- $\text{C}_3\text{N}_4(0.3)$ are shown in Fig. 1(a). In this study, ZIF67- $\text{C}_3\text{N}_4(0.3)$ was chosen as the typical ZIF67- C_3N_4 catalyst

due to its better performance on the photodegradation of MB which will be discussed in Section 3.3. As shown in Fig. 1(a), the diffraction peaks of the black pattern at 7.3°, 10.3°, 12.6°, 17.8°, 24.2°, and 26.4° are assigned to zeolite 4A (Co) (ZIF67, PDF#43-0144) crystal planes of (100), (110), (111), (211), (311), and (320), respectively. This is in line with the former studies [29,36]. For C_3N_4 , which is shown as red pattern in the figure, the diffraction peaks at 15.9° and 27.7° are typically indexed to the crystal planes of (100) and (110) of carbon nitrate (C_3N_4 , PDF#50-1250). Therefore, the expected ZIF67 and C_3N_4 were successfully obtained. The XRD pattern of ZIF67- C_3N_4 (the blue plot in Fig. 1(a)) shows matching diffraction peaks of ZIF67 and C_3N_4 . It is worth noting that the diffraction peak at 27.7° of ZIF67- C_3N_4 was a little wider than that of C_3N_4 . According to the study by Liu and co-workers [29], the strong peak at 27.7° is identified as the conjugated aromatic rings of the interlayer of C_3N_4 . In this case, the insertion of ZIF67 may affect the aromatic rings of C_3N_4 . The FT-IR analysis in Fig. 1(b) revealed that the peaks at 1637 cm^{-1} and 1243 cm^{-1} in the spectrum of C_3N_4 were attributable to the C=N and C-N stretching vibration modes, respectively [16], and the peak at 808 cm^{-1} was related to the s-triazine ring modes. For ZIF67, the peak at 750.5 cm^{-1} was Co-N bond vibration, 1136 cm^{-1} was identified as the peak of C-H bending vibration. The peaks at 1300, 1386 and 1411 cm^{-1} were ascribed to the bending vibration peaks of pyrrole rings. The characteristic peaks of C_3N_4 were all appeared in the FT-IR spectrum of ZIF67- C_3N_4 , and the main peaks of C_3N_4 stretching vibration mode in ZIF67- C_3N_4 were strengthened compared with C_3N_4 (1371, 1300, 1105 and 1040 cm^{-1}), which could be caused by the interaction between the C_3N_4 and ZIF67 [17,18,37].

To study the chemical composition and the existence of C, N and Co in C_3N_4 , ZIF67, and ZIF67- C_3N_4 , the XPS measurement was conducted. Fig. 2(a) displays a full survey of C_3N_4 , ZIF67, and ZIF67- C_3N_4 , and it is obvious that C 1s, N 1s, O 1s, and Co 2p peaks were involved in ZIF67- C_3N_4 . For the high-resolution spectrum of Co 2p (Fig. 2(c)), two main peaks at 782.4 and

Fig. 1. XRD patterns (a) and FTIR plots (b) of C_3N_4 , ZIF67, and ZIF67- $\text{C}_3\text{N}_4(0.3)$.

Fig. 2. (a) XPS full survey; (b) Co 2p spectra of C_3N_4 , ZIF67, and ZIF67- C_3N_4 (0.3); High resolution of Co 2p (c), C 1s (d), and N 1s (e) spectra.

797.7 eV are assigned to Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively [37]. In addition, two distinct satellite peaks of Co $2p_{3/2}$ and Co $2p_{1/2}$ main peaks are located at about 787.3 eV (Sat.a) and 803.6 eV (Sat.b), respectively. This can be further proved by the fitting results of XPS narrow spectra in Fig. 2(c). As reported by the former publications, the energy gap of Co(II) cation corresponds to ca. 6.0 eV, while the Co(III) cation typically features the energy gap to 9–10 eV [17,46]. In this case, Co(II) is the main form existing in the as-prepared ZIF67. There is no significant change in N 1s for the three samples. It is worth noting that the peaks of C 1s for C_3N_4 were different from that of ZIF67- C_3N_4 . As shown in Fig. 2(d), two main peaks of C_3N_4 were detected at 288.3 and 284.7 eV, which correspond to N=C-N₂ and C-C, respectively. By comparison, the intensity of N=C-N₂ in ZIF67- C_3N_4 fell off, while the intensity of C-C was increased

greatly. The main reason could be the superposition of the C-C bond between C_3N_4 and ZIF67.

The SEM images of the C_3N_4 , ZIF67, and ZIF67- C_3N_4 are presented in Fig. 3(a)–(c). It can be seen that C_3N_4 shows irregular structure while ZIF67 consists of polyhedral structure. As presented in the inset of Fig. 3(b), the average size of the polyhedral structure is about 350 nm. As reported by Qian et al. [30], they synthesized ZIF67 through a hydrothermal method and the SEM image of the products showed a polyhedral shape with a particle size of 78 to 385 nm. Therefore, the synthesis method used in this study was successful to prepare ZIF67 with good structure. When it comes to ZIF67- C_3N_4 (Fig. 3(c)), it is obviously that ZIF67 particles were distributed on the surface of the C_3N_4 structure evenly. The TEM images of the three samples are given in Fig. 3(d)–(f), and it can be clearly seen that

Fig. 3. SEM images of C_3N_4 (a), ZIF67 (b), and ZIF67- C_3N_4 (0.3) (c); TEM images of C_3N_4 (d), ZIF67 (e), and ZIF67- C_3N_4 (0.3) (f).

Fig. 4. N₂ adsorption and desorption isotherms (a), and pore size distributions (b) of C₃N₄, ZIF67, ZIF67-C₃N₄(0.3).

raw C₃N₄ shows flaky structures and the ZIF67 particles successfully loaded on the C₃N₄ (Fig. 3(f)).

To investigate the pore structure of the synthesized samples, the N₂ adsorption-desorption test was performed on C₃N₄, ZIF67, and ZIF67-C₃N₄(0.3), and the results are shown in Fig. 4. Obviously, all of the three samples show a type IV adsorption-desorption isotherm (Fig. 4(a)) based on the International Union of Pure and Applied Chemistry (IUPAC) classification [38]. The specific surface area of C₃N₄, ZIF67, and ZIF67-C₃N₄(0.3) are 97.291, 609.225 and 541.392 m²/g, respectively. Therefore, the insertion of ZIF67 significantly increased the specific surface area of C₃N₄, and thus there is a great increase in the total amount of catalytically active sites [34].

The pore structures of the samples are summarized in Table 1 and the BJH adsorption and desorption summary are listed in Table S1. The pore size of the three samples is dominated by mesopores with the diameter ranging from 2 to 8 nm (Fig. 4(b)). Some of the pores appeared as macropores in C₃N₄ and ZIF67-C₃N₄(0.3). This is because there are mesopores in raw C₃N₄, and the mesopores in the ZIF67-C₃N₄(0.3) are then formed by interlayer stacking [29,39].

3.2. Photocatalytic activities

To evaluate the adsorption performance of the photocatalysts, the batch adsorption tests were performed on C₃N₄, ZIF67, and ZIF67-C₃N₄(0.3), respectively. As shown in Fig. S1, about 13% of MB was adsorbed by C₃N₄ at about 10 min. After that, the adsorbed MB started to desorb, and the desorbing

process lasted for about 50 min. The final adsorption efficiency of MB by C₃N₄ was less than 15%. For ZIF67, it is obvious that the MB adsorption by ZIF67 was much higher than that of C₃N₄. The maximum adsorption efficiency of MB by ZIF67 was about 41% obtained at 40 min. Similar to that of C₃N₄, there was a desorption process for ZIF67 between 10 to 20 min. When it comes to ZIF67-C₃N₄(0.3), the adsorption efficiency of MB was about 35% after 60 min. In general, the adsorption performance of MB by the three photocatalysts follows the order of ZIF67 > ZIF67-C₃N₄(0.3) > C₃N₄ which is identified to the specific surface area order of them. As reported by the former study, the removal of dye by C₃N₄ was controlled by two processes: adsorption and photodegradation [40]. The photodegradation of dye can be further divided into two parts: a) photodegradation of dye in the solution, and b) photodegradation of adsorbed dye on C₃N₄ surface. In addition, the adsorption kinetic rate was faster than that of photodegradation and, the photodegradation of adsorbed dye was faster than that in the bulk solution. Therefore, it is expected that the increase in the adsorption capacity of the ZIF67-C₃N₄(0.3) can improve the photodegradation apparent rate constant of the pollutants.

3.2.1. Photocatalytic performance of the catalysts

To examine the enhancement of insertion of ZIF67 to C₃N₄ on the photodegradation of MB, the removal of MB by C₃N₄, ZIF67, ZIF67-C₃N₄ and the direct photolysis of MB under visible light were performed. The photodegradation apparent rate constant of the MB with the presence of different catalysts was determined based on the Langmuir-Hinshelwood equation, which is shown in the Eq. (2) [41–43]:

$$r = -\frac{dC}{dt} = -\frac{k_{obs} \cdot K_L \cdot C}{1 + K_L \cdot C} \quad (2)$$

Where r is the rate of photodegradation of MB (mol/(L·min)), k_{obs} is the apparent degradation rate constant (mol/(L·min)), C is the concentration of MB (mol/L), and K_L is the Langmuir adsorption constant (M⁻¹). When the concentration of MB (C) is extreme low (< 10⁻³ mg/L), Eq. (2) can be fur-

Table 1

Surface area and pore structure of C₃N₄, ZIF67 and ZIF67-C₃N₄(0.3).

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
C ₃ N ₄	97.291	1.096	4.507
ZIF67	609.225	3.909	2.566
ZIF67-C ₃ N ₄ (0.3)	541.372	7.205	5.324

ther simplified as follows:

$$r = -dC/dt = -k_{\text{obs}} \times K_L \times C \quad (3)$$

In the above equation, C can be explained as:

$$C = -kC_0 \times e^{-k't} \quad (4)$$

$$\ln C/C_0 = -k't \quad (5)$$

where C_0 is the initial concentration of MB (mg/L), k' is the constant of pseudo-first-order rate of photodegradation (min^{-1}), and t is the photodegradation time (min).

As shown in Fig. 5(a), MB can degrade itself under visible light with an apparent rate constant of 0.004 min^{-1} which is in line with the former study [44]. With the addition of C_3N_4 , the removal efficiency of MB increased significantly as compared to the direct degradation by visible light. One thing that should be noted is that the photodegradation of MB obviously occurred with the presence of ZIF67. As shown in Fig. 5(a), the removal efficiency of MB increased dramatically to a maximum value of about 76% after 140 min. It could be attributed to the mesoporous structure and large surface area of ZIF67 which allowed the adsorption of MB onto its surface and thus, improve the photodegradation apparent rate constant of the MB by visible light due to the co-called Adsorb & Shuttle process [52]. This is in line with the former study by Luo et al. [40]. The similar phenomenon was also observed by Liu et al. [29], in which the authors studied the photocatalytic removal of NO and stated that the increased catalytic performance of C_3N_4 was caused by the chemical adsorption of NO gas by the hollow structure of ZIF67. When it comes to ZIF67- C_3N_4 , the removal efficiency of MB was greatly improved. The apparent rate constant of MB by ZIF67- C_3N_4 was about 0.029 min^{-1} , which was higher than that of ZIF67 and C_3N_4 (0.011 and 0.014 min^{-1} , respectively). More importantly, the photocatalytic reaction was accelerated and the MB was removed completely by the time of 140 min. This is mainly caused by the photoactive sites on the ZIF67- C_3N_4 is much more than that of raw C_3N_4 .

3.2.2. Effect of C_3N_4 loading amount in ZIF67- C_3N_4

To examine the potential impact of the dosage of C_3N_4 in ZIF67- C_3N_4 composite on the photodegradation of MB, five different ZIF67- C_3N_4 composites were prepared and named as

ZIF67- $\text{C}_3\text{N}_4(0.1)$, ZIF67- $\text{C}_3\text{N}_4(0.2)$, ZIF67- $\text{C}_3\text{N}_4(0.3)$, ZIF67- $\text{C}_3\text{N}_4(0.4)$, and ZIF67- $\text{C}_3\text{N}_4(0.5)$. The numbers in the parentheses represent the amount of C_3N_4 involved in ZIF67- C_3N_4 composites. The photodegradation performance of MB by the above five ZIF67- C_3N_4 is given in Fig. 6. As can be seen in Fig. 6(a), the removal efficiency of MB increased rapidly in the first 10 min of the reaction for all of the five catalysts. This is mainly due to the adsorption of the MB by the catalysts. After that, the C/C_0 curves for ZIF67- $\text{C}_3\text{N}_4(0.1)$, ZIF67- $\text{C}_3\text{N}_4(0.4)$, and ZIF67- $\text{C}_3\text{N}_4(0.5)$ basically remained stable and thus, there was a slight increase in the removal efficiency. By comparison, ZIF67- $\text{C}_3\text{N}_4(0.2)$ and ZIF67- $\text{C}_3\text{N}_4(0.3)$ showed continuous removal of MB during the same period (10–20 min). With the reaction time increased from 10 to 80 min, the removal efficiency of MB by ZIF67- $\text{C}_3\text{N}_4(0.1)$, ZIF67- $\text{C}_3\text{N}_4(0.2)$ and ZIF67- $\text{C}_3\text{N}_4(0.3)$ increased significantly to ~72%, ~80%, and ~90%, respectively. For ZIF67- $\text{C}_3\text{N}_4(0.4)$ and ZIF67- $\text{C}_3\text{N}_4(0.5)$, however, the MB removal efficiency increased by less than 15%. This was mainly because with the increase in the dosage of C_3N_4 may reduce the surface areas of ZIF67- C_3N_4 and ZIF67- C_3N_4 and thus, the adsorption capacity of MB was decreased. In this case, the excessive amount of C_3N_4 may lead to a distinct interruption of photodegradation of MB by ZIF67- C_3N_4 . In general, the removal efficiency of MB by the five catalysts followed the order: ZIF67- $\text{C}_3\text{N}_4(0.5) > \text{ZIF67-}\text{C}_3\text{N}_4(0.4) > \text{ZIF67-}\text{C}_3\text{N}_4(0.3) > \text{ZIF67-}\text{C}_3\text{N}_4(0.2) > \text{ZIF67-}\text{C}_3\text{N}_4(0.1)$ when the reaction time was less than 80 min. After that, the removal efficiency of MB by ZIF67- $\text{C}_3\text{N}_4(0.4)$, and ZIF67- $\text{C}_3\text{N}_4(0.5)$ basically no longer increased, while that of ZIF67- $\text{C}_3\text{N}_4(0.1)$ and ZIF67- $\text{C}_3\text{N}_4(0.2)$ maintained slight increase. In contrast, the increase in the removal efficiency by ZIF67- $\text{C}_3\text{N}_4(0.3)$ was considerable. This can also be proved by the apparent rate constant of the catalysts (Fig. 6(b)), the overall apparent rate constant of ZIF67- $\text{C}_3\text{N}_4(0.3)$ was 0.027 min^{-1} , which was much higher than that of the other four catalysts. Actually, as shown in Fig. 6(b), the plot of the apparent rate constant for ZIF67- $\text{C}_3\text{N}_4(0.5)$ did not consist of the Langmuir-Hinshelwood equation ($R^2 < 0.9$). The main reason is that the high content of C_3N_4 will result in an extremely fast adsorption rate in the first

Fig. 5. (a) Photodegradation of MB with the presences of C_3N_4 , ZIF67, and ZIF67- $\text{C}_3\text{N}_4(0.3)$; (b) Apparent rate constants of the photodegradation of MB (reaction conditions: $V_{\text{MB}} = 100 \text{ mL}$, $C_0 = 10 \text{ mg/L}$, $\text{pH} = 8.6$, dosage of catalysts = 0.01 g).

Fig. 6. (a) Effects of C_3N_4 amount involved in ZIF67- C_3N_4 composites on MB degradation; (b) The apparent rate constants of MB under different ZIF67- C_3N_4 composites; (c) Effect of initial concentration of MB on photodegradation; (d) Apparent rate constants of MB under different MB concentration. Reaction conditions: $V_{MB} = 100$ mL, pH = 8.6, dosage of catalyst = 0.01 g.

10 min of the reaction and therefore, the optimal loading amount of C_3N_4 involved in ZIF67 was determined to be 0.3 g.

3.2.3. Effect of initial concentration of MB

Based on the results in section 3.3.2, ZIF67- C_3N_4 (0.3) was chosen as the best catalyst for the study of the effect of the initial concentration of MB on the photodegradation process. The initial concentration of MB was set to 5, 10, 15 and 20 mg/L, respectively, and the results are presented in Fig. 6(c) and Fig. 6(d). As can be seen from Fig. 6(c), when the initial concentration of MB was 20 mg/L, the maximum removal efficiency of MB was less than 90% after 140 min. In contrast, when the concentration of MB reduced to 15 mg/L, the removal efficiency exceeded 92% at 120 min. The experiment using 10 mg/L of MB for the photodegradation test indicated that MB was completely degraded after 120 min. For 5 mg/L, the MB can be completely degraded within 80 min. The apparent rate con-

stants of MB at different concentrations are shown in Fig. 6(d). In general, when the MB concentrations were 20, 15 and 10 mg/L, the apparent rate constants were in accordance with the Langmuir-Hinshelwood equation. In this case, the apparent rate constant of 20, 15 and 10 mg/L MB conform to the following order: $r_{10\text{mg/L}} (0.02665 \text{ min}^{-1}) > r_{15\text{mg/L}} (0.01208 \text{ min}^{-1}) > r_{20\text{mg/L}} (0.01167 \text{ min}^{-1})$. However, the R^2 of the regression line was less than 0.9 when the MB concentration was 5 mg/L, indicating that the degradation of MB by ZIF67- C_3N_4 (0.3) cannot be exactly described by the Langmuir-Hinshelwood equation. The main reason is that MB was quickly adsorbed on ZIF67- C_3N_4 (0.3) and when the reaction time is less than 10 min, the point measured during this time cannot match the latter point due to the influence of the adsorption process.

3.2.4. Effect of pH of MB solution

Since pH is an important factor that may affect the chemical reactions in aqueous solution, in this study, the effect of pH on the photodegradation process of MB by ZIF67- $\text{C}_3\text{N}_4(0.3)$ was investigated at the pH values of 2.5, 5.0, 8.6, 10.5 and 12.0. Among them, pH 8.6 was the original value of the 10 mg/L of MB solution. To achieve the target pH value, 2 M of NaOH and 1 M of HCl were used. As shown in Fig. 7(a), the degradation of MB by ZIF67- $\text{C}_3\text{N}_4(0.3)$ was extremely low at pH = 2.5, and the maximum removal efficiency of MB was less than 25%. When the solution pH increased to 5.0, the removal efficiency of MB was very close to that of the original 10 mg/L of MB solution. By comparison, the MB removal efficiency of MB was significantly increased when the pH increased to 10.5. As it can be seen in Fig. 7(a), over 95% of MB was removed within 40 min at pH = 10.5. When the pH reached 12, the MB can be completely degraded in the first 5 min. Thus, it is reasonable to draw a conclusion that the strong alkaline condition can significantly enhance the removal of MB by ZIF67- $\text{C}_3\text{N}_4(0.3)$. The apparent rate constant of MB under different pH values is presented in Fig. 7(b). Obviously, the degradation of MB at pH of

5.0 and 8.6 conformed to the Langmuir-Hinshelwood equation and the apparent rate constants were 0.027 and 0.019 min^{-1} , respectively. For pH = 10.5 and 12, the degradation of MB was apparently out the step of the Langmuir-Hinshelwood equation. More specifically, the apparent rate constant under these two pH values complied to the Logistic equation, and the details of the expression of the apparent rate constant of the MB were as follows:

$$r_{10.5} = -3.6 + 2.4/[1 + (t/20)^{1.61}] \quad (6)$$

$$r_{12} = -3.1 + 1.7/[1 + (t/3.45)^{6.47}] \quad (7)$$

In general, the change of photocatalytic degradation as a function of pH is mostly due to the surface ionization of photocatalyst particles. At pH less than the pH at the zero-point charge (ZPC), the surface of the photocatalyst is positive due to the adsorption of positive H^+ and after ZPC is negative due to the adsorption of OH^- on the surface. Since MB is a cationic dye (positively charged), a higher attraction between MB and the photocatalyst can be found in alkaline conditions. Therefore, the apparent rate constant under alkaline conditions is much greater than that under neutral conditions. The apparent rate

Fig. 7. (a) Effect of initial pH of the solution on photodegradation of MB; (b) Apparent rate constants of MB under different pH (reaction conditions: $V_{\text{MB}} = 100$ mL, $C_0 = 10$ mg/L, dosage of catalyst = 0.01 g); (c) UV-vis curve of photodegradation of 10 mg/L of MB by ZIF67- C_3N_4 at pH = 8.6; (d) UV-vis curve of photodegradation of 10 mg/L of MB by ZIF67- C_3N_4 at pH = 12.

constant under acidic condition is much lower than that of alkaline conditions and neutral conditions. This is very meaningful because the reaction time was reduced greatly and so did the cost.

3.3. Mechanism analysis of the photodegradation of MB by ZIF67-C₃N₄

Since the photocatalytic performance of C₃N₄-based photocatalysts is controlled by active species (e.g., OH•, O₂•⁻ and hole (h⁺)) [2,45–48], tert-butyl-alcohol (TBA), formic acid (HCOOH) and p-benzoquinone (p-BQ) were employed as the scavenger for OH•, h⁺ and O₂•⁻, respectively. As shown in Fig. 8(a), the

photodegradation of MB was greatly inhibited with the presence of HCOOH, indicating that h⁺ played the key role in the degradation of MB by C₃N₄, ZIF67 and ZIF67-C₃N₄. Besides, the photodegradation of MB by ZIF67-C₃N₄ reduced to some extent after adding p-BQ revealed that O₂•⁻ also participated in the MB degradation. To examine photocurrent response of C₃N₄, ZIF67 and ZIF67-C₃N₄ under visible light, the CHI-760e electrochemical workstation was used. FTO glass deposited with above three photocatalysts, Pb wire, and saturated calomel electrode were used as working electrode, counter electrode and reference electrode, respectively. The electrolyte solution was the 0.1 mol/L Na₂SO₄ solution. The results are presented in Fig. 8(b). It is obvious that the photocurrent of ZIF67-C₃N₄ is much

Fig. 8. (a) Photodegradation of MB with the addition of different scavengers; (b) Transient photocurrent responses of C₃N₄, ZIF67, and ZIF67-C₃N₄ (0.3) under visible light; (c) Schematic illustration of the possible degradation mechanism of MB by ZIF67-C₃N₄ (0.3).

higher than that of raw C_3N_4 , indicating that the improvement of mobility of charge carriers in ZIF67- C_3N_4 [12,16].

To verify the visible light response of bare C_3N_4 , ZIF674 and ZIF67- C_3N_4 , the UV-vis diffuse reflectance spectrum of the catalysts was carried out using U-3900 Spectrophotometer (HITACHI) and the absorption spectrum are presented in Fig. S2. For C_3N_4 , the absorption edge is about 400 nm indicates it can be used to utilize visible light [16]. By comparison, the adsorption edge of ZIF67- C_3N_4 is much wide than that of C_3N_4 when the wavelength is less than 400 nm. More importantly, there is a strong absorption peak at about 600 nm resulting in the improvement of utilization of visible light. Moreover, there is a little increase in band gap energy (E_g) [48–51] of ZIF67- C_3N_4 as compared to C_3N_4 , indicating that the synthesis procedure developed in this article has no damage on the photocatalytic properties of C_3N_4 .

Based on above analysis, the possible mechanism of photodegradation of MB was proposed as Fig. 8(c). Because of the enhancement of adsorption capability, MB was quickly adsorbed and enriched on the surface of ZIF67- C_3N_4 . As a result, the mass transfer distance of the photodegradation process was significantly reduced [53,54]. The adsorbed MB was then in-situ degraded and the time for photodegradation was then reduced greatly. Since the bandgap of ZIF67- C_3N_4 is about 2.75 eV (Fig. S2), it can be induced by visible light to produce holes and electrons [55]. More importantly, the insertion of ZIF67 nanoparticles significantly improved the generation of holes and electrons. The generated holes then served as the main species for MB degradation. Besides, the photo-induced electrons from C_3N_4 reacted with dissolved oxygen in the solution to form superoxide radicals [56], which performed as another active species for MB degradation. In general, the synergistic adsorption and photodegradation process of ZIF67- C_3N_4 can improve the degradation of MB significantly.

4. Conclusions

This article presents a study on the synthesis of zeolite-imidazole framework modified C_3N_4 (ZIF67- C_3N_4) and applied it to the photocatalytic degradation of MB. Results showed that after doping with ZIF67, the specific surface area of the ZIF67- C_3N_4 catalyst increased greatly to a maximum of 609.225 m²/g. As a result, the insertion of ZIF67 can significantly improve the adsorption of MB on the ZIF67- C_3N_4 composite and reduce the photodegradation time. With the addition of 0.01 g ZIF6- C_3N_4 (0.3) composite, a total volume of 100 mL of MB at 10 mg/L was thoroughly degraded in 120 min with an apparent rate constant of 0.028 min⁻¹. In addition, the investigation of the effect of pH on the removal of MB revealed that 100 mL of MB at 10 mg/L can be completely degraded within 10 min at pH = 12. This is very delightful because of the energy-saving derived from the reduction of photocatalysis time. The photo-induced holes (h^+) play a leading role in MB degradation and superoxide radicals ($O_2^{\cdot-}$) generated from the reaction between electrons and dissolved oxygen served as another active species for the photodegradation of MB.

Conflict of Interests

The authors declare no conflict of interest.

References

- [1] K. T. Carvalho, A. E. Nogueira, O. F. Lopes, G. Byzinski, C. Ribeiro, *Cera. Int.*, **2017**, 43, 3521–3530.
- [2] Y. Sheng, Z. Wei, H. Miao, W. Yao, H. Li, Y. Zhu, *Chem. Engineering J.*, **2019**, 370, 287–294.
- [3] S. N. Ahmed, W. Haider, *Nanotechnology*, **2018**, 29, 342001.
- [4] D. B. Miklos, C. Remy, M. Jekel, K. G. Linden, J. E. Drewes, U. Hübner, *Water Res.*, **2018**, 139, 118–131.
- [5] D. S. Babu, V. Srivastava, P. V. Nidheesh, M. S. Kumar, *Sci. Total Environ.*, **2019**, 696, 133961.
- [6] R. Hao, G. Wang, H. Tang, L. Sun, C. Xu, D. Han, *Appl. Catal. B*, **2016**, 187, 47–58.
- [7] C. Pan, J. Jia, X. Hu, J. Fan, E. Liu, *Appl. Surf. Sci.*, **2018**, 430,

Graphical Abstract

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Investigation of surface processes in electrocatalysis by scanning tunneling microscopy

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Uniformly distributed single layer ZIF67-derived C_3N_4 was used to the efficient photocatalytic degradation of methylene blue (MB) under visible light. Results indicated that photo-induced holes (h^+) and superoxide radicals ($O_2^{\cdot-}$) were responsible for MB degradation.

- 283–292.
- [8] Q. Tang, X. Meng, Z. Wang, J. Zhou, H. Tang, *Appl. Surf. Sci.*, **2018**, 430, 253–262.
- [9] Y. Zhang, P. Su, D. Weathersby, Q. Zhang, J. Zheng, R. Fan, J. Zhang, Q. Dai, *Appl. Surf. Sci.*, **2020**, 501, 144217.
- [10] S. Borthakur, L. Saikia, *J. Environ. Chem. Eng.*, **2019**, 7, 103035.
- [11] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.*, **2009**, 8, 76.
- [12] M. Zhang, W. Jiang, D. Liu, J. Wang, Y. Liu, Y. Zhu, Y. Zhu, *Appl. Catal. B*, **2016**, 183, 263–268.
- [13] T. Arumugham, R. G. Amimodu, N. J. Kaleekkal, D. Rana, *J. Environ. Sci.*, **2019**, 82, 57–69.
- [14] J. Fu, J. Yu, C. Jiang, B. Cheng, *Adv. Energy Mater.*, **2018**, 8, 1701503.
- [15] Z. Jiang, W. Wan, H. Li, S. Yuan, H. Zhao, P. K. Wong, *Adv. Mater.*, **2018**, 30, 1706108.
- [16] Y. Wang, R. Shi, J. Lin, Y. Zhu, *Energy Environ. Sci.*, **2011**, 4, 2922–2929.
- [17] Y. He, Y. Wang, L. Zhang, B. Teng, M. Fan, *Appl. Catal. B*, **2015**, 168, 1–8.
- [18] Q. Sun, K. Lv, Z. Zhang, M. Li, B. Li, *Appl. Catal. B*, **2015**, 164, 420–427.
- [19] J. Yan, H. Wu, H. Chen, Y. Zhang, F. Zhang, S. F. Liu, *Appl. Catal. B*, **2016**, 191, 130–137.
- [20] L. Ge, C. Han, J. Liu, *Appl. Catal. B*, **2011**, 108, 100–107.
- [21] J. Wang, L. Tang, G. Zeng, Y. Liu, Y. Zhou, Y. Deng, J. Wang, B. Peng, *ACS Sustainable Chem. Eng.*, **2016**, 5, 1062–1072.
- [22] M. Zhang, Y. Zhang, L. Tang, G. Zeng, J. Wang, Y. Zhu, C. Feng, Y. Deng, W. He, *J. Colloid Interface Sci.*, **2018**, 539, 654–664.
- [23] G. Miao, D. Huang, X. Ren, X. Li, Z. Li, J. Xiao, *Appl. Catal. B*, **2016**, 192, 72–79.
- [24] M. Ou, S. Wan, Q. Zhong, S. Zhang, Y. Song, L. Guo, W. Cai, Y. Xu, *Appl. Catal. B*, **2018**, 221, 97–107.
- [25] Z. Sun, Z. Yu, Y. Liu, C. Shi, M. Zhu, A. Wang, *J. Colloid Interface Sci.*, **2019**, 533, 251–258.
- [26] N. Stock, S. Biswas, *Chem. Rev.*, **2011**, 112, 933–969.
- [27] X. Xu, R. Cao, S. Jeong, J. Cho, *Nano Lett.*, **2012**, 12, 4988–4991.
- [28] W. Chaikittisilp, K. Ariga, Y. Yamauchi, *J. Mater. Chem. A*, **2013**, 1, 14–19.
- [29] D. Liu, D. Chen, N. Li, Q. Xu, H. Li, J. He, J. Lu, *Small*, **2019**, 1902291.
- [30] J. Qian, F. Sun, L. Qin, *Mater. Lett.*, **2012**, 82, 220–223.
- [31] J. Navarro-Sánchez, N. Almora-Barrios, B. Lerma-Berlanga, J. J. Ruiz-Pernía, V. A. Lorenz-Fonfria, I. Tuñón, C. Martí-Gastaldo, *Chem. Sci.*, **2019**, 10, 4082–4088.
- [32] Y. Chen, D. Wang, X. Deng, Z. Li, *Catal. Sci. Technol.*, **2017**, 7, 4893–4904.
- [33] C. Wang, J. Kim, V. Malgras, J. Na, J. Lin, J. You, M. Zhang, J. Li, Y. Yamauchi, *Small*, **2019**, 15, 1900744.
- [34] G. Zhou, M. F. Wu, Q. J. Xing, F. Li, H. Liu, X. B. Luo, J. P. Zou, J. M. Luo, A. Q. Zhang, *Appl. Catal. B*, **2018**, 220, 607–614.
- [35] K. Y. A. Lin, H. A. Chang, *J. Taiwan Inst. Chem. Eng.*, **2015**, 53, 40–45.
- [36] J. S. M. Lee, Y. I. Fujiwara, S. Kitagawa, S. Horike, *Chem. Mater.*, **2019**, 31, 4205–4212.
- [37] Y. Pan, K. Sun, S. Liu, X. Cao, K. Wu, W. C. Cheong, Z. Chen, Y. Wang, Y. Li, Y. Liu, D. Wang, Q. Peng, C. Chen, Y. Li, *J. Am. Chem. Soc.*, **2018**, 140, 2610–2618.
- [38] L. Shang, H. Yu, X. Huang, T. Bian, R. Shi, Y. Zhao, G. I. N. Waterhouse, T. Zhang, *Adv. Mater.*, **2016**, 28, 1668–1674.
- [39] Z. Mao, J. Chen, Y. Yang, D. Wang, L. Bie, B. D. Fahlman, *ACS Appl. Mater. Interfaces*, **2017**, 9, 12427–12435.
- [40] Y. Luo, X. Wei, B. Gao, W. Zou, Y. Zheng, Y. Yang, Y. Zhang, Q. Tong, L. Dong, *Chem. Eng. J.*, **2019**, 122019.
- [41] G. W. Roberts, C. N. Satterfield, *Ind. Eng. Chem. Fund.*, **1965**, 4, 288–293.
- [42] N. G. Asenjo, R. Santamaria, C. Blanco, M. Granda, P. Alvarez, R. Menéndez, *Carbon*, **2013**, 55, 62–69.
- [43] Y. Deng, *Chem. Eng. J.*, **2018**, 337, 220–227.
- [44] J. Tang, Z. Zou, J. Yin, J. Ye, *Chem. Phys. Lett.*, **2003**, 382, 175–179.
- [45] S. C. Yan, Z. S. Li, Z. G. Zou, *Langmuir*, **2010**, 26, 3894–3901.
- [46] Q. Xiang, J. Yu, M. Jaroniec, *J. Phys. Chem. C*, **2011**, 115, 7355–7363.
- [47] W. J. Ong, L. L. Tan, Y. H. Ng, S. T. Yong, S. P. Chai, *Chem. Rev.*, **2016**, 116, 7159–7329.
- [48] Y. Feng, S. Lin, S. Huang, S. Shrestha, G. Conibeer, *J. Appl. Phys.*, **2015**, 117, 125701.
- [49] P. Soni, V. V. S. Murty, K. K. Kushwaha, *J. Nanosci. Nanoeng. Appl.*, **2018**, 8, 69–74.
- [50] F. Wei, Z. Deng, S. Sun, N. T. P. Hartono, H. L. Seng, T. Buonassisi, P. D. Bristowe, A. K. Cheetham, *Chem. Commun.*, **2019**, 55, 3721–3724.
- [51] R. Su, Q. Li, Y. Chen, B. Gao, Q. Yue, W. Zhou, *J. Cleaner Prod.*, **2019**, 209, 20–29.
- [52] R. Djellabi, M. F. Ghorab, A. Smara, C. L. Bianchi, G. Cerrato, X. Zhao, B. Yang, In: *Green Materials for Wastewater Treatment*, M. Naushad, E. Lichtfouse, eds., Springer, **2020**, 291–319.
- [53] Q. Hao, Y. Huang, D. Chen, Y. Liu, W. Wei, B. J. Ni, *Chin. J. Catal.*, **2020**, 41, 249–258.
- [54] Q. Hao, G. Jia, W. Wei, A. Vinu, Y. Wang, H. Arandian, B. J. Ni, *Nano Res.*, **2020**, 13, 18–37.
- [55] J. Qian, F. Sun, L. Qin, *Mater. Lett.*, **2012**, 82, 220–223.
- [56] S. C. Yan, Z. S. Li, Z. G. Zou, *Langmuir*, **2009**, 25, 10397–10401.

单层ZIF67纳米颗粒修饰的C₃N₄在可见光下光催化降解有机污染物

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摘要: 随着全球工业化水平的提高, 有机污染物引起的水环境问题也日益严重. 针对有机污染物表现出的持久性和难降解性等问题, 全球科研工作者提出了不同的方法去治理相关环境问题. 其中利用光催化降解有机污染物作为一种新兴技术, 因处理成本低、污染物降解效率高、光催化剂可回收利用等优点受到越来越多的关注. 在诸多的光催化剂中, 氮化碳(C₃N₄)拥有2.7 eV的能带宽度, 且其合成简单, 价格低廉, 环境友好, 以及在可见光下即可催化降解污染物等特点而被广泛研究. 但是, 比表面积小和易与光激发电荷载流子结合等缺点也制约C₃N₄的广泛应用. 针对上述问题, 本文将具有巨大比表面积

的金属骨架材料ZIF67引入到 C_3N_4 之中, 合成了均匀分布的单层ZIF67衍生的 C_3N_4 (ZIF67- C_3N_4), 并将其应用于可见光下的亚甲基蓝(MB)光催化降解. 结果表明, 所制得的ZIF67- C_3N_4 的最大比表面积可达 $541.392\text{ m}^2/\text{g}$, 远高于未加工的 C_3N_4 的 $97.291\text{ m}^2/\text{g}$. ZIF67- C_3N_4 光催化活性结果表明, 2.57 g ZIF67和 0.3 g C_3N_4 即ZIF67- C_3N_4 (0.3)表现出优异的光催化活性. 加入 0.01 g 的ZIF67- C_3N_4 (0.3)可以在 70 min 内降解90%以上的浓度为 10 mg/L 的亚甲基蓝, 而原 C_3N_4 在同等条件下处理相同浓度的亚甲基蓝所需的时间超过 140 min . 同时, 本文还考察了溶液的pH值, 亚甲基蓝的初始浓度和ZIF67- C_3N_4 复合材料中 C_3N_4 的含量等因素对亚甲基蓝光催化降解的影响. 结果显示, ZIF67- C_3N_4 (0.3)在碱性条件下降解亚甲基蓝的效率高于中性条件. 在 $\text{pH} = 12$ 的情况下, ZIF67- C_3N_4 (0.3)可以在 10 min 内完全降解 100 mL 的浓度为 10 mg/L 的亚甲基蓝. 此外, 在酸性条件下亚甲基蓝的降解效果很差, 说明ZIF67- C_3N_4 (0.3)在酸性条件下容易失活. 通过对亚甲基蓝初始浓度对光催化反应的研究显示, 当亚甲基蓝的初始浓度为 20 mg/L 时, 经 140 min 反应后, 亚甲基蓝的去除率小于90%; 当亚甲基蓝的浓度降至 15 mg/L 时, 其在 120 min 的降解效率超过92%; 而 10 mg/L 的亚甲基蓝可在 120 min 内完全降解. 对制备的五种催化剂对亚甲基蓝的降解效果分析得出ZIF67- C_3N_4 (0.3)比其他四种催化剂的效果更好. 为了揭示ZIF67- C_3N_4 (0.3)在可见光条件下催化降解亚甲基蓝的反应机理, 本文利用叔丁醇、甲酸以及对苯醌进行淬灭实验. 结果表明, 光致空穴(h^+)和超氧自由基($O_2^{\cdot-}$)是降解亚甲基蓝的主要活性物质.

关键词: 金属有机骨架结构; 光催化; C_3N_4 ; ZIF67; 可见光

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