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Article (Special Issue on Environmental and Energy Catalysis for Sustainable Development)

Simultaneous formation of a C/N-TiO₂ hollow photocatalyst with efficient photocatalytic performance and recyclability

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ARTICLE INFO

Article history:

Received 22 October 2018

Accepted 17 December 2018

Published 5 May 2019

Keywords:

Simultaneous synthesis

C/N-doped TiO₂

Hollow sphere

Tetracycline

Photocatalysis

ABSTRACT

Herein, we report a unique approach towards the preparation of C-modified and N-doped TiO₂ hollow spheres (C/N-TiO₂). TEM, SEM, and XPS analyses were used to confirm that the carbon and nitrogen co-decorated TiO₂ photocatalyst was formed. Carbon-decoration improves the visible-light absorption and speeds up the separation of the photo-generated electron-hole pairs. C/N-TiO₂ not only narrows the band gap of TiO₂, but also exhibits excellent photocatalytic activity for the degradation of tetracycline and tetracycline hydrochloride. In addition, the C/N-TiO₂ photocatalyst shows excellent recyclability for water decontamination, making it a promising candidate to purify aquatic contaminants.

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1. Introduction

Efficiently removing dissolved organic compounds is a major challenge in remediation water treatment [1–3]. Photocatalysis is considered as a promising tool to purify aquatic contaminants because it can result in the complete photodestruction of these contaminants [3,4]. Among them, TiO₂-based photocatalysts are extremely photocatalytic materials due to their excellent advantages, which include strong oxidative power, low cost, and stability [3,5]. However, the photocatalytic efficiency of TiO₂-based materials is not up to the mark to meet out the practical needs because of their wide band gap and fast electron-hole (e⁻/h⁺) pair recombination [3,5]. To overcome these disadvantages, persistent efforts have been focused on changing the composition of TiO₂ by introducing impurities

that produce donor or acceptor states in the band gap [5–7]. However, metal-doped TiO₂ usually exhibits low thermal stability and photo-corrosion [5]. Whereas, non-metal doping shows more potential towards improving the visible-light absorption properties compared with metal decoration [3,5]. For example, N-doped TiO₂ has been shown to drive the spectral response of TiO₂ into the visible-light region because the N2p states contribute to the band gap [8,9]. Zeng and co-workers [10] developed N-doped TiO₂, which displayed high visible-light photoactivity for the degradation of phenol and benzene. Wang et al. [11] prepared TiO₂ nanowire arrays via nitrogen implantation, which exhibited significantly enhanced visible light photoactivity. However, multi-step procedures are required to prepare N-doped TiO₂ using traditional methods [12]. In addition, the stability of N-doping is poor under visi-

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This work was supported by the National Natural Science Foundation of China (21876069, 21707054), the Six Talent Peaks Project in Jiangsu (XCL-018), and the China Postdoctoral Science Foundation (2016M601744).

DOI: S1872-2067(19)63286-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 5, May 2019

ble-light irradiation because of the low concentration of the nitrogen dopant [13]. On the other hand, carbon-decoration has great potential towards achieving a high level of visible-light performance because carbon materials can act as efficient trapping centers for photo-generated electrons [5,7,13]. Moreover, carbon displays strong visible-light absorption properties, which facilitate e^-/h^+ pair transfer from TiO_2 to the pollutant molecules [5,14]. Kim et al. [15] prepared mesoporous carbon- TiO_2 via a soft-template-carbonization route, which achieved good visible-light efficiency towards the decomposition of p-nitrophenol. Recently, our group has introduced an *in situ* synthesis of C-doped TiO_2 photocatalysts and the as-synthesized SiO_2 @C-doped TiO_2 showed enhanced visible-light and UV-light performance for the degradation of Rhodamine B (RhB) [5]. However, the performance of single-doped/decorated TiO_2 is still below that required for the efficient use of solar light because the strategies used to prepare single-doped TiO_2 materials containing a high dopant concentration are scarce [13,16,17]. Therefore, novel strategies for the preparation of visible-light responsive TiO_2 with high performance are still urgently required.

Compared to single doping/decoration, co-doping has attracted a considerable attention to improve the visible-light performance of TiO_2 photocatalysts due to its synergistic effect [18,19]. Xu et al. [20] synthesized carbon-decorated and N-doped TiO_2 nanoparticles with high visible-light photoactivity. Vaiano et al. [21] developed a phosphor modified N-doped TiO_2 (NdT/OP) photocatalyst, which can be used to degrade various organic dyes under visible-light irradiation. Li et al. [13] introduced a range of carbon/N-doped TiO_2 photocatalysts and showed that the co-decorated TiO_2 materials have increased visible-light photoactivity for the decomposition of RhB. However, the addition of carbon precursors (e.g., chitosan [13], L-lysine [20], etc.) is necessary in the preparation of carbon-doped TiO_2 , as reported in the literature. Specifically, low-surface area TiO_2 nanoparticles/powder are used as the matrix in most of the previously reported studies [10,13,16,19,20,22,23], which significantly impair the photocatalytic efficiency and recovery observed in photocatalytic water decontamination and other applications.

In this study, we introduce a cost-effective technique for the simultaneous synthesis of carbon-modified and N-doped TiO_2 (C/N- TiO_2) hollow spheres. The C/N- TiO_2 photocatalyst not only overcomes the disadvantages of multi-step strategies because it is simultaneously prepared via the pyrolysis of a polystyrene template under an NH_3/Ar atmosphere, but also exhibits a uniform shape, controlled pore size and shell thickness, which improve the photocatalytic performance. Moreover, the band gap of TiO_2 was reduced to ~ 2.83 eV, whilst the carbon-decoration improves the visible-light absorption properties and efficiently separates the e^-/h^+ pairs. In addition, the hollow structure of C/N- TiO_2 with high surface area is able to boost the diffusion of reactants by decreasing the diffusion resistance and enhancing the accessibility, which results in an enhanced visible-light/simulated solar light efficiency.

2. Experimental

2.1. Materials

Tetrabutylorthotitanate (TBT) was obtained from J&K Chemical Company Ltd and used without any further purification. Styrene, $\text{K}_2\text{S}_2\text{O}_8$, ammonia, ethanol, tetracycline (TC), and tetracycline hydrochloride (TC-HCl) were purchased from Sinopharm Chemical Reagent Co., Ltd (China), in which styrene was purified using NaOH solution (5 wt%). P25 nanoparticles (Degussa) and 2-(methacryloyloxy)ethyltrimethylammonium chloride (DMC) were purchased from Sigma-Aldrich Ltd. Deionized water was used in all our experiments.

2.2. Simultaneous synthesis of the C/N- TiO_2 hollow spheres

Cationic polystyrene spheres (CPS) were synthesized according to our previous works [24–26]. An ethanol solution of CPS (0.1 g/mL, 40 mL) was added to a 100-mL three-necked flask, and an ethanol solution of TBT (0.1 g/mL, 20 mL) was slowly added to the reaction vessel under ice bath. Subsequently, $\text{NH}_3/\text{H}_2\text{O}$ was added to the reaction mixture to give the CPS@ TiO_2 precursor. The resulting solid was separated, washed, dried, and calcined under an NH_3/Ar atmosphere at 450 °C [10], simultaneously forming the carbon-modified, N-doped TiO_2 (C/N- TiO_2) hollow spheres.

2.3. Characterization of the C/N- TiO_2 hollow spheres

Transmission electron microscopy (TEM), scanning electron microscopy (SEM), and STEM mapping were used to characterize the structure and morphology of the C/N- TiO_2 hollow spheres. In addition, Brunauer-Emmett-Teller (BET) method (TriStar II 3020) was employed to obtain the surface area and porosity. The crystal phases of C/N- TiO_2 and commercial P25 were analyzed using X-ray diffraction (XRD). X-ray photoelectron spectroscopy (XPS) was used to analyze the surface properties.

2.4. Measurement of the photocatalytic activity

The photocatalytic activity of the C/N- TiO_2 hollow spheres was investigated using the decomposition of TC and TC-HCl. 50 mL of an aqueous solution containing TC and TC-HCl (10 mg/L) and the photocatalyst (0.5 mg/L) was subjected to visible light ($\lambda > 420$ nm) and simulated solar light (300 W Xe lamp equipped with an AM 1.5 filter) irradiation, respectively. Prior to irradiation, the photocatalytic system was stirred for 30 min in the absence of light to reach equilibrium. At given time intervals, ~ 4 mL of the suspension was removed from the reaction system, centrifuged, and measured using UV-visible absorption spectroscopy ($\lambda_{\text{TC}} = 357$ nm). To measure the recyclability, the used C/N- TiO_2 catalyst was recycled as follows. After the photocatalytic test, the C/N- TiO_2 photocatalyst was recovered via simple filtration, dried at room temperature, and reused in the next cycle.

3. Results and discussion

Scheme 1. An illustration of the process used to prepare the C/N-TiO₂ hollow spheres.

3.1. Synthesis of the C/N-TiO₂ hollow spheres

Scheme 1 illustrates the preparation of the carbon-modified, N-doped hollow TiO₂ spheres (C/N-TiO₂). CPS was prepared via an emulsion-free polymerization reaction [24–26]. TBT was slowly added to the CPS solution followed by the dropwise addition of NH₃/H₂O to produce the CPS@TiO₂ precursor. The precursor was calcined at 450 °C under an NH₃/Ar atmosphere to remove the CPS template and produce the carbon-modified, N-doped TiO₂ hollow spheres (C/N-TiO₂).

TEM and SEM were used to characterize the structure and morphology of the as-synthesized C/N-TiO₂ hollow spheres. The TEM images indicate that the C/N-TiO₂ was hollow and porous in nature, as shown in Fig. 1(a) [5]. In particular, the almost uniform shells suggest that this synthesis technique can maintain the porosity and hollow structure during the phase transition of TiO₂, which is undoubtedly a decisive factor that affects the photocatalytic activity of the TiO₂ photocatalyst [27]. The SEM image of several broken spheres confirms the hollow nature of the C/N-TiO₂ spheres, as shown in Fig. 1(b).

EDX analysis of the C/N-TiO₂ sample was used to measure the chemical composition. Clear signals for Ti, O, C, and N were observed in the EDX survey spectrum (Fig. 2(a)), suggesting the existence of C and N species in the TiO₂ [28]. Fig. 2(c) also shows that the N signal is dispersed throughout hollow spheres, whereas the C signal (Fig. 2(f)) is mostly present on the outer layer of the hollow TiO₂ spheres, suggesting the successful integration of the different components in the C/N-TiO₂ hollow spheres. The N₂ adsorption-desorption isotherms show the same condensation steps appear in the relative pressure range of 0.1–1.0, which indicates an ordered porous structure, as illustrated in Fig. 3(a). The BET specific area of the C/N-TiO₂

Fig. 1. TEM (a) and SEM (b) images of the C/N-TiO₂ hollow spheres.

Fig. 2. EDX survey spectrum (a), STEM image (b) and EDX mapping of the C/N-TiO₂ hollow spheres. (c) N; (d) Ti; (e) O; (f) C.

hollow spheres was found to be high (up to 108.6 m²/g) according to the N₂ adsorption-desorption isotherms, and was more than two-times larger than that observed for commercial P25 (50.2 m²/g, Fig. 3(b)). This enhanced surface area improves the diffusion of the reactants by decreasing the diffusion resistance.

3.2. Crystal phase and binding energy of the C/N-TiO₂ hollow spheres

Fig. 4 indicates that the distinctive reflection peaks for TiO₂ observed at 25.4° (101), 37.9° (004), 48.0° (200), 54.9° (211) and 62.8° (204) can be attributed to the anatase form (JCPDS:

Fig. 3. BET isotherms and BJH pore size distribution (inset) of the C/N-TiO₂ hollow spheres (a) and the BET isotherms of commercial P25 (b).

Fig. 4. XRD spectra recorded for the C/N-TiO₂ hollow spheres, anatase TiO₂ and commercial P25 samples.

No 21-1272) [5,29]. No amorphous or other polymorphs (e.g., rutile or brookite) were observed in the XRD spectrum, suggesting the formation of anatase crystals via the carbonization of CPS at 450 °C under an NH₃/Ar atmosphere.

Fig. 5(a) shows that O, Ti, N, and C were present according to their binding energies, indicating that the C/N-TiO₂ hollow spheres include N, C, and TiO₂. In the Ti 2p spectrum, the characteristic peak at 464.29 eV was indexed to Ti 2p_{1/2} and the

other peak observed at 458.41 eV corresponds to Ti 2p_{3/2}, as shown in Fig. 5(b). Furthermore, the Ti2p_{3/2} peak of C/N-TiO₂ was positively shifted by 0.17 eV (458.41 eV) when compared to the Ti 2p_{3/2} peak observed at 458.24 eV in the spectrum of commercial P25. The Ti 2p_{1/2} binding energy of the commercial P25 sample was observed at 463.96 eV, which was again observed at an enhanced binding energy (0.33 eV) in the C/N-TiO₂ hollow spheres. Clearly, the positive shift can be ascribed to the strong interactions formed between Ti⁴⁺ and the C and N elements [18], indicating the presence of lattice distortion in the C/N-TiO₂ hollow spheres [5,18]. In addition, Fig. 5(c) shows that the O 1s peaks were observed at 529.97 and 532.82 eV. Compared with the O 1s spectrum of the commercial P25 sample, a clear positive shift was observed in the O1s spectrum of the C/N-TiO₂ hollow spheres, suggesting the existence of oxygen vacancies [3,5].

Fig. 5(d) shows the high-resolution N1s spectrum of the C/N-TiO₂ hollow spheres. A broad peak was observed from 396 to 403 eV, which corresponds to the characteristic peak of N-doped TiO₂, as reported in the literature [1,9,15]. After fitting the curve, four peaks at 398.4, 399.43, 401.15, and 401.89 eV were observed for N-TiO₂ and N-TiO_{2-x}, which are consistent with the N1s binding energy region and hollow TiO₂@N-doped carbon [8,9,30]. Fig. 5(e) shows the C1s spectrum of the C/N-TiO₂ hollow spheres, which can be fitted into three peaks at 285.24, 286.56, and 289.53 eV, suggesting the existence of carbon in three different chemical environments. The peak observed at 285.24 eV corresponds to residual elemental car-

Fig. 5. (a) XPS survey spectrum of the C/N-TiO₂ hollow spheres and the corresponding Ti 2p (b), O 1s (c), N 1s (d), and C 1s (e) spectra.

Fig. 6. UV-vis absorption spectra (a) and band gap energy (b) of the C/N-TiO₂ hollow spheres and commercial P25 sample.

bon, which acts as a photo-sensitizer to enhance the visible-light absorption of the C/N-TiO₂ hollow spheres [31,32]. The two characteristic peaks observed at 286.56 and 289.53 eV were assigned to the existence of oxygen bound species [9,30,31]. Therefore, the XPS measurements confirm the formation of carbon-modified, N-doped TiO₂ hollow spheres via the pyrolysis of CPS under an NH₃/Ar atmosphere.

3.3. Absorbance spectra and band gap of the C/N-TiO₂ hollow spheres

As shown in Fig. 6(a), it is clear that commercial P25 only absorbs UV light because of its wide band gap [1,5]. In contrast, the C/N-TiO₂ photocatalyst not only displays a strong UV light response, but also exhibits a wide visible-light response. Obviously, the visible-light absorption can be ascribed to the co-decoration of TiO₂ by N and C, which results in a dramatic enhancement in its visible-light absorption properties [1,5]. The band gap energy (E_g) values for commercial P25 and the C/N-TiO₂ hollow spheres were calculated according to Kubelka-Munk method, as shown in Fig. 6(b) [13]. Excitedly, C/N-co-doping was able to narrow the band gap energy (2.83 eV) of the C/N-TiO₂ photocatalyst, which facilitates the excitation of the electrons in C/N-TiO₂ under visible-light irradiation and thus, leads to its enhanced photocatalytic efficiency.

3.4. Synthesis of the C/N-TiO₂ hollow spheres with tunable shell thickness

The shell thickness of the C/N-TiO₂ hollow spheres was easily controlled by varying the amount of TBT precursor used [33], as shown in Fig. 7. When 2 g of TBT was used, the C/N-TiO₂ hollow spheres have a shell thickness of 15 nm determined from the cross-sectional TEM images of the sample obtained using digital micrograph software (Fig. 7(a)). When 3 g of TBT was added, an enhanced shell thickness (~22 nm) was obtained, as shown in Fig. 7(b). When 4 g of TBT was added, the shell thickness of the C/N-TiO₂ hollow spheres was ~29 nm. Moreover, we further measured the effect on the surface area when increasing the amount of TBT used. Figs. 3 and 8 show that the surface area of the three C/N-TiO₂ samples was

108.6, 70.6, and 53.3 m²/g when using 2, 3, and 4 g of TBT, respectively. In addition, the BET isotherms demonstrate that the shell thickness does not significantly change the adsorption type, pore structure and size of the C/N-TiO₂ hollow spheres. Therefore, the shell thickness (15–29 nm) of the C/N-TiO₂ hollow spheres can be easily controlled by changing the amount of TBT added during their synthesis.

3.5. Photocatalytic activities of the C/N-TiO₂ hollow spheres

Simultaneous modification/doping can significantly enhance the photocatalytic activity of TiO₂ because of its synergistic effect. In this work, we have demonstrated its applicability for the decomposition of antibiotics under visible-light and simulated solar light irradiation. Single-decorated TiO₂ (e.g.,

Fig. 7. TEM and SEM images of the C/N-TiO₂ hollow spheres prepared using 2 g (a,b), 3 g (c,d), and 4 g (e,f) of TBT.

Fig. 8. BET isotherms of the C/N-TiO₂ hollow spheres prepared using 3 g (a) and 4 g (b) of TBT.

carbon-modified hollow TiO₂ (C/TiO₂) was used as a reference photocatalyst under the same experimental conditions.

Fig. 9 shows the visible-light catalytic performance of the

photocatalysts [C/TiO₂ and C/N-TiO₂] for the degradation of tetracycline (TC). As shown in Fig. 9(a), with the increase of illumination time, the characteristic absorption band of TC

Fig. 9. Photocatalytic performance of the TC (a), C/TiO₂ (b) and C/N-TiO₂ (c) photocatalysts for the degradation of TC under visible-light irradiation.

(~357 nm) does not exhibit any obvious change in the absence of a photocatalyst. After the addition of the C/TiO₂ photocatalyst, the characteristic absorption band of TC decreases gradually upon visible-light irradiation (Fig. 9(b)), indicating that the C/TiO₂ photocatalyst can effectively speed up the degradation of TC. In contrast, a faster decrease in the characteristic absorption band of TC was observed for the as-synthesized C/N-TiO₂ photocatalyst, as shown in Fig. 9(c). The time course for the decrease in the TC concentration using the photocatalysts is shown in Fig. 9(d). Tetracycline (TC) itself cannot be degraded under visible-light irradiation. In the presence of a photocatalyst, the as-synthesized C/N-TiO₂ photocatalyst can degrade 86.3% of TC, which is beyond the TC degradation value (76.4%) of the C/TiO₂ photocatalyst within 30 min after irradiation. The enhanced visible-light photocatalytic performance was also further confirmed by degrading tetracycline hydrochloride (TC-HCl) using the two photocatalysts (C/TiO₂ and C/N-TiO₂) under the same photocatalytic conditions, as shown in Fig. 10.

The degradation of TC was further investigated using the two photocatalysts under simulated solar light irradiation, as shown in Fig. 11. Compared with the visible-light removal rate

of TC, the degradation value of TC was increased to 23.1% after 30 min of irradiation. In contrast, the removal rate of TC using C/TiO₂ was increased to 98.3% under the same photocatalytic conditions. However, the as-synthesized C/N-TiO₂ photocatalyst exhibited an TC removal efficiency of 99.6%, indicating that the TC was almost completely degraded under simulated solar light irradiation. Based on the previously reported studies [34,35], the degradation of pollutants can be attributed to a pseudo-first-order reaction using the simplified Langmuir-Hinshelwood model when C_0 is very low.

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

where, k and C are the apparent first-order rate constant and concentration of TC in solution at a certain time, respectively. The degradation of TC is slow using C/TiO₂ with a rate constant (K_a) of 0.1311 min⁻¹, whereas the as-synthesized C/N-TiO₂ hollow spheres further improve the degradation rate of TC to $K_a = 0.1812$ min⁻¹, which approaches a 1.4-fold increase than C/TiO₂. Obviously, N-doping plays an important role in improving the degradation rate of TC. The enhanced photocatalytic efficiency was further confirmed by the decomposition of tetracycline hydrochloride (TC-HCl), as demonstrated in Fig. 11(c) and (d). All the data strongly confirm that co-decoration

Fig. 10. Photocatalytic performance of the TC-HCl (a), C/TiO₂ (b) and C/N-TiO₂ (c) photocatalysts for the degradation of TC-HCl under visible-light irradiation.

Fig. 11. Photocatalytic performance of the C/TiO₂ and C/N-TiO₂ photocatalysts towards the degradation of TC and TC-HCl under simulated solar-light irradiation.

improves the photocatalytic performances of TiO₂ due to the synergistic effect [18,19], as expected.

3.6. The effect of the shell thickness on the visible light photocatalytic activity of the C/N-TiO₂ hollow spheres

In order to achieve the optimal photocatalytic activity, the most suitable shell thickness needs to be determined. Fig. 12 indicates the photocatalytic performance of the three representative C/N-TiO₂ hollow spheres towards the degradation of TC under visible light and simulated solar light irradiation. Specifically, when the shell thickness was ~15 nm (C/N-TiO₂-2TBT), the highest photocatalytic activity was observed. When the thickness was increased to ~22 nm (C/N-TiO₂-3TBT), a slightly decreased degradation of TC was observed. When shell thickness was further increased to ~29 nm (C/N-TiO₂-4TBT), the degradation rate of TC further decreases accordingly. This trend was mainly attributed to the decreased surface area (Fig. 8) indicating that an optimal shell thickness was important for the C/N-TiO₂ hollow spheres because it offers more space and active sites for the adsorption of TC.

3.7. Photodegradation mechanism of TC

To elaborate the increased photocatalytic performance of the C/N-TiO₂ hollow spheres, we have proposed a possible mechanism for the degradation process. When the oxygen atoms are replaced with nitrogen atoms, a new impurity level is formed between the valence and conduction band of TiO₂. Under visible-light irradiation, the electrons are excited to the conduction band of TiO₂ from the impurity level (~2.83 eV) [1,36]. In addition, the carbon-coating can exhibit many advantages including the enhanced adsorption of TC or TC-HCl, efficient electron trapping, and decreased charge transfer resistance [2,7]. Therefore, the excellent photocatalytic behavior can be ascribed to the synergistic effect of the nitrogen and carbon species in the as-synthesized C/N-TiO₂ hollow spheres.

The photodegradation of TC exhibits a typical ·OH oxidation mechanism and pathway because larger intermediates with an $m/z = 461$ produced via the hydroxylation reaction are detected in this study [37,38], as shown in Fig. 13. The product with $m/z = 445$ was ascribed to the molecular weight of TC [39]. After TC was attacked by ·OH, intermediate 1 ($m/z = 461$) was

Fig. 12. Photocatalytic performance of the C/N-TiO₂ hollow spheres with different shell thickness towards the degradation of TC under visible light (a) and simulated solar-light (b) irradiation.

Fig. 13. The possible photodegradation pathways for the degradation of TC.

produced. Subsequently, the N-methyl groups are gradually cleaved to generate intermediates 2 ($m/z = 430$) and 3 ($m/z = 416$). Because the amino group and carbocyclic ring in intermediate 3 was further lost to produce intermediate 4 ($m/z = 345$), intermediate 4 could be further oxidized to form intermediates 5 ($m/z = 303$) [40] and 6 ($m/z = 276$). Intermediate 7 ($m/z = 136$) is also detected because of the cleavage of the carbocyclic ring. CO₂, H₂O and inorganic ions are ultimately formed in the presence of the C/N-TiO₂ photocatalyst.

3.8. Recyclability of the C/N-TiO₂ photocatalyst

A series of recycling experiments were carried out for the decomposition of TC under visible-light irradiation using the C/N-TiO₂ photocatalyst in order to evaluate its potential application [2,41,42]. Four consecutive recycling runs shows that the as-synthesized C/N-TiO₂ photocatalyst exhibits an almost unchanged degradation rate during the four consecutive runs

(Fig. 14), indicating its high recyclability for the treatment of wastewater [2,41]. Clearly, the good durability is able to be responsible for the unique synergistic effect of C and N species in the TiO₂ hollow spheres.

4. Conclusions

In summary, we have devised a novel strategy to prepare a carbon-modified and N-doped TiO₂ hollow photocatalyst. The pore size and shell thickness C/N-TiO₂ are readily controlled by the CPS template and tuning the amount of TBT precursor used. After carbonization of the CPS template under an NH₃/Ar atmosphere at 450 °C, the nitrogen element is doped in the place of oxygen, simultaneously forming the C-modified and N-doped anatase TiO₂ hollow spheres. The results confirm that the N-doping has been formed and the carbon species were decorated on the surface of the photocatalyst, narrowing the band gap of TiO₂, and enhancing the visible-light absorption of

Fig. 14. The recycling experiment of the decomposition of TC using the C-N/TiO₂ photocatalyst under visible light irradiation.

TiO₂. Therefore, when the C/N-TiO₂ hollow spheres were employed as a photocatalyst for the decomposition of TC and TC-HCl, and the C/N-TiO₂ photocatalyst showed an enhanced efficiency when compared to C/TiO₂. Specifically, the C/N-TiO₂ photocatalyst showed excellent recyclability for water decontamination, which considerably increased its potential for actual application in industry.

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Graphical Abstract

Chin. J. Catal., 2019, 40: 765–775 doi: S1872-2067(19)63286-9

Simultaneous formation of a C/N-TiO₂ hollow photocatalyst with efficient photocatalytic performance and recyclability

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Carbon-modified and N-doped TiO₂ (C/N-TiO₂) was simultaneously synthesized. The photocatalytic properties can be adjusted by changing the shell thickness of the C/N-TiO₂ hollow spheres. C/TiO₂ shows enhanced photocatalytic performance for the degradation of tetracycline.

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碳-氮共改性中空二氧化钛光催化剂的同步合成及其高效的光催化行为和循环稳定性研究

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摘要: 抗生素的滥用导致了严重的水体污染, 如何处理水体中难以降解的抗生素是目前环境领域中重要的研究课题之一。研究发现, 二氧化钛具有优良的光催化性能, 但由于其宽能带(~3.2 eV), 导致其低抗生素的降解率。本文构建了一种新型的碳氮共改性中空二氧化钛光催化剂(C/N-TiO₂), 研究发现, 所制备的C/N-TiO₂不仅能提高二氧化钛的可见光吸收, 而且还有效地降低了其禁带宽度, 因此能大大地提高其对四环素的降解能力和降解速率。该新型的C/N-TiO₂光催化剂主要利用阳离子聚苯乙烯作为创造二氧化钛中空结构的模板和碳源, 在氨/氩混合气作用下煅烧, 能同步制备出碳-氮共改性的中空二氧化钛光催化剂。TEM和SEM电镜图清晰显示出C/N-TiO₂具有良好的中空结构。STEM Mapping测试证实碳和氮元素都均匀地分布在C/N-TiO₂的中空微球上, 实现了其良好的改性。N1s的XPS谱图显示出在N-TiO₂和N-TiO_{2-x}的特征峰的存在, 证实了氮掺杂TiO₂的成功合成。固体紫外也进一步证实了C/N-TiO₂不仅具有强的紫外光吸收, 还因碳和氮共改性呈现出强的可见光吸收。更重要的是, 这种碳/氮共改性有效地降低了TiO₂的禁带宽度(~2.83 eV)。

研究了C/N-TiO₂光催化剂在可见光和模拟太阳光作用下, 对四环素类的光催化降解行为, 并与碳改性的中空二氧化钛(C/TiO₂)的进行比较。结果表明, 在可见光作用下, C/N-TiO₂光催化剂在30 min内能降解大约86.3%四环素, 高于C/TiO₂对四环素(76.4%)。在可见光降解氯四环素时, C/N-TiO₂也取得了比C/TiO₂更高的降解率。我们进一步测试了两种催化剂在模拟太阳光作用下的催化性能差异。结果表明, C/TiO₂对四环素降解率达到98.3%, 而C/N-TiO₂在30 min内几乎实现了四环素的完全降解(99.6%)。根据Langmuir-Hinshelwood计算出四环素的降解速率, 发现C/N-TiO₂对四环素的降解速度为0.1812 min⁻¹, 是同样条件下C/TiO₂的1.4倍。结果表明, 所研制的C/N-TiO₂无论是在可见光还是在模拟太阳光作用下, 都比C/TiO₂展现出更高的四环素和氯四环素的降解率。以上结果清晰的表明碳氮共改性因其协同效应, 比碳改性在提高TiO₂的催化性能方面起着更重要的作用。

本文用质谱进一步研究了四环素光降解的中间体, 并提出了其可能的降解路径。光催化循环实验证明, 所制备的C/N-TiO₂在循环四次后, 其对四环素的降解率都没有发生明显的下降, 说明C/N-TiO₂具有良好的循环稳定性, 为其潜在的应用奠定了坚实的基础。

关键词: 同步合成; 碳氮共改性二氧化钛; 中空微球; 四环素; 光催化作用

收稿日期: 2018-10-22. 接受日期: 2018-12-17. 出版日期: 2019-05-05.

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基金来源: 国家自然科学基金(21876069, 21707054); 江苏省“六大人才”高峰计划(XCL-018); 中国博士后基金(2016M601744).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).