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Article

Defect-assisted surface modification enhances the visible light photocatalytic performance of g-C₃N₄@C-TiO₂ direct Z-scheme heterojunctions

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ABSTRACT

To increase the number of active sites and defects in TiO₂ and promote rapid and efficient transfer of photogenerated charges, a g-C₃N₄@C-TiO₂ composite photocatalyst was prepared via in situ deposition of g-C₃N₄ on a carbon-doped anatase TiO₂ surface. The effects of carbon doping state and surface modification of g-C₃N₄ on the performance of g-C₃N₄@C-TiO₂ composite photocatalysts were studied by X-ray diffraction, X-ray photoelectron spectroscopy, UV-visible diffuse-reflectance spectroscopy, transmission electron microscopy, electrochemical impedance spectroscopy, photoluminescence, and electron paramagnetic resonance. With increasing carbon doping content, the carbon doping state in TiO₂ gradually changed from gap to substitution doping. Although the number of oxygen vacancies gradually increased, the degradation efficiency of g-C₃N₄@C-TiO₂ for RhB (phenol) initially increased and subsequently decreased with increasing carbon content. The g-C₃N₄@10C-TiO₂ sample exhibited the highest apparent reaction rate constant of 0.036 min⁻¹ (0.039 min⁻¹) for RhB (phenol) degradation, which was 150 (139), 6.4 (6.8), 2.3 (3), and 1.7 (2.1) times higher than that of pure TiO₂, 10C-TiO₂, g-C₃N₄, and g-C₃N₄@TiO₂, respectively. g-C₃N₄ was grown in situ on the surface of C-TiO₂ by surface carbon hybridization and bonding. The resultant novel g-C₃N₄@C-TiO₂ photocatalyst exhibited direct Z-scheme heterojunctions with non-local impurity levels. The high photocatalytic activity can be attributed to the synergistic effects of the improved visible light response ability, higher photogenerated electron transfer efficiency, and redox ability arising from Z-type heterojunctions.

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1. Introduction

Photocatalytic technology is a promising method for solving various energy and environmental problems [1–3]. Among the many developed photocatalysts, TiO₂ and g-C₃N₄ have shown

excellent prospects in the fields of solar energy utilization and environmental protection because of their unique physical and chemical properties [4–10]. Compared with single photocatalytic materials, composite photocatalysts can improve quantum efficiency, increase specific surface area, promote sufficient

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contact between the catalyst surface and reactant molecules, and improve the separation efficiency of photogenerated electron-hole pairs. For example, the band structure of TiO_2 and $\text{g-C}_3\text{N}_4$ matches to a significant degree. In addition, the catalytic activity of the heterojunction composites is greatly enhanced when irradiation with ultraviolet or visible light [11–15].

Directly combining bulk $\text{g-C}_3\text{N}_4$ with other materials often results in small specific surface area and insufficient interface contact, limiting carrier migration between the two materials. Therefore, the abovementioned advantages of composite materials are not always fully realized. Researchers have improved the activity of $\text{g-C}_3\text{N}_4$ using various methods including fabrication of $\text{g-C}_3\text{N}_4$ nanotubes [16,17], nanorods [18,19], nanofibers [20], and nanosheets [21–23], coupled with direct mixing with TiO_2 to prepare composites. Yu et al. [24] used a chemical formation method, as opposed to the more common physical methods, to prepare a Z-scheme $\text{g-C}_3\text{N}_4/\text{TiO}_2$ system. The Z-scheme $\text{g-C}_3\text{N}_4/\text{TiO}_2$ heterojunction was fabricated by calcining a mixture of TiO_2 and urea. Subsequently, $\text{g-C}_3\text{N}_4$ was grown in situ on the surface of the TiO_2 particles.

Construction of high catalytic activity carbon-doped TiO_2 (C- TiO_2) is a popular research topic in the field of environmental photocatalysis [25–30]. However, significant drawbacks exist for traditional C- TiO_2 preparation methods, such as the need for additional carbon sources and carbon component aggregation. Thus, it is necessary to continuously optimize existing methods and design novel strategies for preparing multifunctional carbon-doped TiO_2 composite materials. To the best of our knowledge, few studies have considered the effects of the carbon doping state on TiO_2 photocatalytic activity or the synergistic effects of defect-assisted surface modification by in situ deposition of $\text{g-C}_3\text{N}_4$ on the photocatalytic performance of $\text{g-C}_3\text{N}_4/\text{C-TiO}_2$ heterojunctions.

To increase the number of active sites and defects in the TiO_2 material and achieve rapid and efficient transfer of photogenerated charges, a one-step hydrothermal method was used for in situ preparation of nano-carbon-doped TiO_2 to increase oxygen vacancy defects and surface active sites. A simple chemical vapor deposition method was subsequently used to crack urea through furnace heating. The effects of the carbon doping state and synergistic effects of surface modification by in situ deposition of $\text{g-C}_3\text{N}_4$ on the performance of the $\text{g-C}_3\text{N}_4/\text{C-TiO}_2$ composite photocatalysts were investigated.

2. Experimental

2.1. Preparation of the photocatalyst

C- TiO_2 (anatase) was synthesized using a hydrothermal combined calcination method. First, 3 mL of TiCl_4 was dissolved in 70 mL of glycol with concentrations of 5, 10, and 20 g/L. To the mixed solution, 2 mL of ammonia was added under magnetic stirring for 30 min to ensure complete hydrolysis. Subsequently, 5 mL of 0.01 g/mL glucose solution was added dropwise and left to stir for 1 h. The obtained mixture was subjected to hydrothermal treatment at 150 °C for 10 h. After centrifugation, washing, and drying, the precursor was prepared. The

C- TiO_2 nanoparticle powder was obtained after the precursor was calcined at 450 °C for 3 h, where 5C- TiO_2 , 10C- TiO_2 , and 20C- TiO_2 represent carbon-doped anatase obtained using glucose concentrations of 5, 10, and 20 g/L, respectively. For comparison, pure TiO_2 and $\text{g-C}_3\text{N}_4$ samples were prepared where pure TiO_2 was prepared by the solvothermal method. A suitable amount of TiCl_4 was mixed with 70 mL of ethylene glycol and 2 mL ammonia was added dropwise to the mixed solution under magnetic stirring. Afterwards, the mixture was stirred for 1 h and placed in a hydrothermal kettle for reaction at 150 °C for 10 h. After the reaction was complete, the precipitate was filtered and washed three times with water and ethanol. The precipitate was then dried at 80 °C for 12 h. Finally, the dried powder was heated to 450 °C for 5 h at a heating rate of 5 °C/min, resulting in an anatase-phase TiO_2 solid. Nanoporous $\text{g-C}_3\text{N}_4$ was prepared via pyrolysis of an aqueous urea solution, as described in detail in previous studies [9,13]. Urea and distilled water were mixed in a mass ratio of 3:4 to form the aqueous urea solution, which was then placed in a corundum crucible with a cover and calcined at 400 °C for 1 h and subsequently at 500 °C for 2 h at a heating rate of 15 °C/min.

The C- TiO_2 powder was dispersed on a protruding platform in the corundum crucible and urea was uniformly spread on the bottom of the crucible. The covered corundum crucible was placed in a rapid heating sintering furnace, calcined at 400 °C for 1 h, and then heated to 500 °C for 2 h at a heating rate of 15 °C/min. After cooling, the $\text{g-C}_3\text{N}_4/\text{C-TiO}_2$ composite photocatalyst was obtained. For comparison, a $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (without carbon) sample was prepared using a similar process. A schematic diagram of the preparation process is shown in Fig. 1.

2.2. Characterization

The phase composition of the obtained samples was characterized by X-ray diffractometry (XRD, D8 Advance, Bruker, Germany) using a $\text{Cu K}\alpha$ radiation source. The microstructures and element mapping of the prepared samples were observed by transmission electron microscopy (TEM, Talos F200X, FEI, USA) equipped with an energy dispersive spectrometer (EDS). X-ray photoelectron spectroscopy (XPS) analysis was performed (Axis Ultra DLD, Shimadzu, Japan) with monochromatized $\text{Al K}\alpha$ radiation. The UV-visible diffuse reflection spectra (DRS) were recorded using a UV-visible spectrophotometer (UV-3150, Shimadzu, Japan) equipped with an integrating sphere. The photoelectrochemical properties of the samples were characterized using an electrochemical analyzer (CHI660E, Shanghai Chenhua, China) with a three-electrode system. ITO glass substrate with a photocatalyst film (20 mg), calomel electrode, and Pt wire were served as the working, reference, and counter electrodes, respectively. A Na_2SO_4 solution (0.5 mol/L) was used as the electrolyte solution. Photoluminescence (PL) spectra were obtained using a fluorescence spectrophotometer (F-7000, Hitachi, Japan) at room temperature. Electron paramagnetic resonance (EPR) spectroscopy was performed using an EPR spectrometer (JES FA200, JEOL Ltd., Japan).

Fig. 1. Schematic diagram of the preparation process of samples.

2.3. Photocatalytic activity measurement

The photocatalytic activities of the samples were tested by decomposing Rhodamine B (RhB) and phenol pollutants in an aqueous solution under visible-light. A 350-W xenon arc lamp with a UV-cutoff filter ($\lambda > 420$ nm) was placed into a double-wall cylindrical quartz reactor with a water circulator. The composite photocatalyst powder (100 mg) was suspended in 100 mL of RhB or phenol solution (10 mg/L). The suspensions were magnetically stirred in the dark for 1–2 h to establish adsorption-desorption equilibrium before irradiation. For the photocatalytic activity test, approximately 5 mL of the mixture was collected every 0.5 h and centrifuged for 10 min at 9000 rpm to remove the photocatalyst. The supernatant was then analyzed using a UV-visible spectrophotometer (UV-3150, Shimadzu, Japan) and the characteristic absorption peaks were evaluated. The removal rates of RhB and phenol were calculated from the absorbance according to the Beer-Lambert law. The detection process of the active species was similar to that of the photocatalytic performance testing. Ammonium oxalate (AO, h^+ capture agent), isopropyl alcohol (IPA, $\cdot OH$ capture agent), and benzoquinone (BQ, $\cdot O_2^{-1}$ capture agent) were added to the photocatalytic reaction system to determine the active species in the photocatalytic process.

2.4. Theoretical calculations

First-principles calculations were performed to investigate the electronic structure of the carbon-doped TiO_2 using the Vienna Ab initio Simulation Package (VASP) based on density functional theory (DFT) [31,32]. The exchange correlation functional was introduced by the generalized gradient approximation (GGA) of Perdew-Berke-Ernzerhof (PBE) [33,34]. A $2 \times 2 \times 1$ supercell with 48 atoms was used for the doped TiO_2 . In the supercell, 1 oxygen atom was substituted by a carbon atom and simultaneously formed a single oxygen vacancy. To examine the concentration of carbon atoms, 2 oxygen atoms were substituted by a single carbon atom and 1 oxygen vacancy in the supercell. All plane waves with a cutoff energy of 400 eV

were used in the basis function. The convergence criteria for structural and energy optimization at each atom were set as 0.01 eV/Å and 10^{-6} eV, respectively.

3. Results and discussion

3.1. Crystal structure and chemical state of the surface elements

The XRD patterns obtained from the pure TiO_2 , 5C- TiO_2 , 10C- TiO_2 , 20C- TiO_2 , and g- C_3N_4 @10C- TiO_2 samples are shown in Fig. 2. The crystal structure of TiO_2 (anatase) was not changed by the combination of carbon and g- C_3N_4 and no obvious carbon peaks were observed in the samples, indicating that carbon was doped into the anatase crystals. Fig. 2(b) shows a partially enlarged view of the 23° – 27° diffraction angle, where all C- TiO_2 samples were shifted to a lower angle. This indicated that some carbon was doped in the interstitial space in anatase, leading to increased interplanar spacing. However, as the carbon content increased, the diffraction peaks of 10C- TiO_2 and 20C- TiO_2 were not further shifted to lower angle, indicating that carbon may be doped in the form of lattice position substitution. In addition, the angle of the g- C_3N_4 @10C- TiO_2 composite was shifted to a higher angle. The stress induced by the interaction of g- C_3N_4 and 10C- TiO_2 may have led to the deformation and shrinkage of the TiO_2 lattice during thermal deposition.

To further confirm the chemical state of carbon on the surface of TiO_2 , XPS characterization of the C- TiO_2 samples was performed. Fig. 3 shows the XPS spectra of the 5C- TiO_2 , 10C- TiO_2 , and 20C- TiO_2 samples. It could be seen from the carbon peaks in Fig. 3(a)–(c) that the peak intensity of the adsorbed C-C and C-OH bonds formed after pyrolysis of the organic matter on the surface of TiO_2 increased with increasing carbon content. This indicated that the amount of carbon adsorbed on the surface increased with increasing concentration of the organic precursor. The Ti-C bond formed by substitution of the lattice oxygen position with carbon followed the same trend. However, the peak intensity of the O-C bond formed by carbon gap doping initially increased with increasing carbon content and then plateaued. These results showed that when

Fig. 2. (a) XRD patterns of obtained pure TiO_2 , 5C- TiO_2 , 10C- TiO_2 , 20C- TiO_2 and $\text{g-C}_3\text{N}_4@10\text{C-TiO}_2$ samples; (b) corresponding XRD patterns in a narrow 2θ of samples.

Fig. 3. XPS spectra of C 1s of 5C- TiO_2 (a), 10C- TiO_2 (b) and 20C- TiO_2 (c), and Ti 2p of 5C- TiO_2 , 10C- TiO_2 and 20C- TiO_2 (d).

the carbon content was increased to a certain level, the carbon-doped TiO_2 gradually changed from gap to substitution doping modes. The Ti 2p peak in Fig. 3(d) further supports the above conclusion. That is to say, with increasing carbon doping content, the peak strength of the Ti-C peak gradually increased and the corresponding peak intensity of the Ti-O peak gradually decreased, indicating that carbon replaced the position of oxygen in the lattice.

3.2. Light absorption performance, band gap energy, and microstructure

The UV-vis DRS of the pure TiO_2 , 5C- TiO_2 , 10C- TiO_2 ,

20C- TiO_2 , $\text{g-C}_3\text{N}_4@5\text{C-TiO}_2$, $\text{g-C}_3\text{N}_4@10\text{C-TiO}_2$ and $\text{g-C}_3\text{N}_4@20\text{C-TiO}_2$ samples are shown in Fig. 4. As the carbon content increased, the absorption edge of C- TiO_2 was significantly red-shifted and absorbance was enhanced. When combined with $\text{g-C}_3\text{N}_4$, the red shift of the absorption edge was more dramatic, especially for the $\text{g-C}_3\text{N}_4@10\text{C-TiO}_2$ sample. This indicated that the $\text{g-C}_3\text{N}_4@10\text{C-TiO}_2$ sample exhibited improved visible light response. The band gap energy (E_g) of the C- TiO_2 samples were calculated using the Tauc/Davis-Mott expression, as shown in Fig. 4(b). The band gap of C- TiO_2 gradually decreased with increasing carbon doping content, which also explained the red shift of the absorption edge.

The microstructures of the $\text{g-C}_3\text{N}_4@10\text{C-TiO}_2$ material were

Fig. 4. UV-vis DRS (a) and plots of $(\alpha h\nu)^2$ vs E_g (b) of different samples.

characterized by TEM and element mapping was achieved using EDS, as shown in Fig. 5. The black C-TiO₂ nanoparticles with a diameter of 20–30 nm were surrounded by a thin layer of g-C₃N₄. As seen in the HRTEM image (Fig. 5(b)), the thin g-C₃N₄ layer was tightly coated around the C-TiO₂ nanoparticles, indicating that the C-TiO₂ nanoparticles were successfully surface-modified, which improved the transmission of photogenerated carriers. In addition, the lattice fringes of TiO₂ exhibited significant defects (indicated by the red circle in Fig. 5(b)), mainly due to interstitial carbon doping. In the HRTEM image in Fig. 5(c) most of the TiO₂ lattice fringes were arranged regularly. However, a small number of defects were found in the middle of the periodically arranged lattice fringes (as shown in the dotted box), indicating the presence of partial oxygen vacancies in C-TiO₂. From the electron diffraction pattern in Fig. 5(d), it was determined that g-C₃N₄@10C-TiO₂ exhibited a polycrystalline structure. The element mappings of the rectangular frame shown in Fig. 5(a) are displayed Fig. 5(e)–(h), corresponding to C, N, O, and Ti, respectively. These maps further demonstrate that carbon and g-C₃N₄ were successfully incorporated into the g-C₃N₄@10C-TiO₂ composites.

3.3. Photocatalytic activity

The photocatalytic activities of the pure TiO₂, g-C₃N₄, g-C₃N₄@TiO₂, g-C₃N₄@5C-TiO₂, g-C₃N₄@10C-TiO₂, and g-C₃N₄@20C-TiO₂ samples were examined for their RhB and phenol photodegradation ability under visible-light irradiation (Fig. 6). The g-C₃N₄@C-TiO₂ sample exhibited higher photocatalytic degradation efficiency than those of the pure TiO₂, g-C₃N₄, and g-C₃N₄@TiO₂ samples (without carbon). With increasing carbon content, the photocatalytic degradation efficiency of g-C₃N₄@C-TiO₂ initially increased and subsequently decreased. Calculation of the Langmuir-Hinshelwood mechanism (shown in Fig. 6(b) and (d)) showed that g-C₃N₄@10C-TiO₂ exhibited the largest apparent constant (k) of 0.036 and 0.039 min^{−1} for RhB and phenol photodegradation, respectively, which was 150/139, 6.4/6.8, 2.3/3.0, and 1.7/2.1 times higher than those of pure TiO₂, 10C-TiO₂, g-C₃N₄, and g-C₃N₄@TiO₂, respectively. For comparison, the degradation rates and k values for RhB and phenol degradation by the as-prepared samples and other reported photocatalysts are

Fig. 5. TEM (a) and HRTEM (b,c) and electron diffraction pattern (d); element mappings of C (e), N (f), O (g) and Ti (h) elements.

Fig. 6. Time-course variation of C/C_0 (a) and $\ln(C_0/C)$ (b) curves for RhB degradation; time-course variation of C/C_0 (c) and $\ln(C_0/C)$ (d) curves for phenol degradation; UV-vis absorption spectra of RhB (e) and phenol (f) solution in the presence of $g-C_3N_4@10C-TiO_2$ in different degradation time; cycling runs of the photocatalytic degradation for RhB (g) and phenol (h).

listed in Table 1 [35–38].

The UV-vis absorption spectra (Fig. 6(e) and (f)) of the RhB and phenol solutions in the presence of $g-C_3N_4@10C-TiO_2$ under visible-light irradiation show that the intensity of the RhB and phenol absorption peaks gradually decreased with increasing degradation time and were gradually blue-shifted, indicating that the photocatalyst induced mineralization and decomposition of the organic pollutants. The degradation cycle performance (Fig. 6(g)) of RhB and phenol (inserted image) by $g-C_3N_4@10C-TiO_2$ showed that the degradation activity towards RhB and phenol did not decrease significantly after four cycles, indicating good cyclic stability.

3.4. Photocatalytic mechanism

To test the photocharge transfer efficiency of the catalyst,

the sample was measured using impedance spectroscopy and the results are shown in Fig. 7(a). Similar to the photocatalytic degradation activity, the $C-TiO_2$ samples exhibited small impedance values, with $g-C_3N_4@10C-TiO_2$ exhibiting the lowest impedance, indicated that it had a higher photogenerated electron transfer efficiency. The PL spectra of the as-prepared pure $g-C_3N_4$, $g-C_3N_4@TiO_2$, $g-C_3N_4@5C-TiO_2$, $g-C_3N_4@10C-TiO_2$, and $g-C_3N_4@20C-TiO_2$ are shown in Fig. 7(b). Compared to pure $g-C_3N_4$, $g-C_3N_4@TiO_2$, $g-C_3N_4@5C-TiO_2$, and $g-C_3N_4@20C-TiO_2$, $g-C_3N_4@10C-TiO_2$ exhibited the lowest peak intensity, indicating that it had the lowest charge recombination probability. From the EPR spectra (shown in Fig. 7(c)), it is clear that the peak intensity gradually increased with increasing carbon content, which can be attributed to the formation of oxygen vacancies by carbon reduction and doping. The active species capture experiment confirmed that $\cdot OH$ and $\cdot O_2^-$ radicals were the

Table 1

The degradation rates and k values for RhB (phenol) degradation by as-prepared samples and other reported photocatalysts.

Sample	Degradation rate (%)	Degradation time (min)	k (min^{-1})	Ref.
$g-C_3N_4@10C-TiO_2$	~97	90	0.036 (RhB)	This work
$g-C_3N_4@10C-TiO_2$	~92	60	0.039 (phenol)	This work
$g-C_3N_4/MoS_2$	~99	12	0.3 (RhB)	[35]
$g-C_3N_4/WO_3$	~92	120	– (RhB)	[36]
N-doped graphene/ Ag_2CO_3	~90	25	0.093 (phenol)	[37]
$g-C_3N_4/Bi_2O_3$	~32	150	– (phenol)	[38]

Fig. 7. EIS (a), PL (b), and EPR (c) spectra of TiO_2 , $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4/\text{TiO}_2$, $\text{g-C}_3\text{N}_4/5\text{C-TiO}_2$, $\text{g-C}_3\text{N}_4/10\text{C-TiO}_2$ and $\text{g-C}_3\text{N}_4/20\text{C-TiO}_2$ samples; active species capture experiment (d).

Fig. 8. The band structure of TiO_2 (a), 10C-TiO_2 (b), 20C-TiO_2 (c).

dominant in the RhB and phenol degradation by $\text{g-C}_3\text{N}_4/10\text{C-TiO}_2$, while the h^+ radical was less significant (Fig. 7(d)).

To further investigate the effects of carbon doping on the band structure of TiO_2 , the energy band structures of TiO_2 and C-TiO_2 were calculated from first principles, the results of which are shown in Fig. 8. The band gap between the conduction and valence bands of the pure TiO_2 was empty. Some impurity energy levels were introduced between the conduction and valence bands when a certain amount of carbon was doped. However, when carbon doping was excessive, the Fermi level of the 20C-TiO_2 sample passed through the conduction band and the impurity level was localized, which hindered

electron transfer [39]. This phenomenon may be caused by excessive carbon doping leading to the formation of bulk oxygen vacancies, which can easily bind photogenerated electrons and became recombination centers for photogenerated carriers.

The formation mechanism of the $\text{g-C}_3\text{N}_4/\text{C-TiO}_2$ composite and its mechanism of influence on electron transfer are shown in Fig. 9(a). According to the experimental results, in addition to the solid solution of carbon atoms in the TiO_2 lattice by substitution and interstitial doping, some carbon atoms were adsorbed on the TiO_2 surface via C-C and C-OH bonding. Therefore, $\text{g-C}_3\text{N}_4$ was tightly bound to the surface of C-TiO_2 by π -conjugate and hydrogen bonding. Photogenerated electrons

Fig. 9. (a) Proposed schematics of formation and electron transfer mechanism of $\text{g-C}_3\text{N}_4/\text{C-TiO}_2$ composite; (b) photocatalytic mechanism of $\text{g-C}_3\text{N}_4/\text{C-TiO}_2$ heterojunction.

in the g-C₃N₄@C-TiO₂ composite were susceptible to electron transport through internal doping and surface hybridized carbon atoms. The proposed schematic of the photocatalytic mechanism for the g-C₃N₄@C-TiO₂ heterojunction is shown in Fig. 9(b). Based on the results described above, it can be concluded that the most likely mechanism for the g-C₃N₄@C-TiO₂ heterojunction was a direct Z-scheme mechanism. There are two main reasons for this. First, the active species for RhB and phenol degradation by g-C₃N₄@10C-TiO₂ are ·OH and ·O₂^{·-}. Only h⁺ on the valence band of C-TiO₂ can produce ·OH, while the oxidation ability of h⁺ on the valence band of g-C₃N₄ is insufficient to form ·OH. Therefore, the holes cannot migrate from the valence band of C-TiO₂ to the valence band of g-C₃N₄ and remain in their original position with a higher oxidation potential to produce ·OH. Second, the Fermi level of the surface of C-TiO₂ is lower than that of g-C₃N₄. Therefore, when C-TiO₂ and g-C₃N₄ are combined, an inherent electric field from g-C₃N₄ to C-TiO₂ forms between the g-C₃N₄@C-TiO₂ heterojunctions [39,40]. The holes in the valence band of C-TiO₂ cannot move to the valence band of g-C₃N₄ because of rejection by the built-in electric field. In contrast, the electrons on the C-TiO₂ conduction band can migrate to the valence band of g-C₃N₄ owing to the attraction of the inherent electric field, forming a direct Z-type heterojunction. The presence of a certain amount of surface oxygen vacancies in C-TiO₂ can generate a new defect level, which can effectively separate and transfer electron-hole pairs to the catalyst surface. The highly conductive carbon connecting TiO₂ and g-C₃N₄ can transfer electrons rapidly to the valence band of g-C₃N₄, which forms a direct Z-type photocatalytic heterojunction. This significantly improves the separation and transfer efficiency of photogenerated carriers and photocatalytic activity of the g-C₃N₄@C-TiO₂ heterostructured photocatalysts.

4. Conclusions

In summary, g-C₃N₄@carbon-doped anatase TiO₂ heterostructure photocatalysts were prepared by a facile hydrothermal combined vapor deposition method. With increasing carbon content, the diffraction peaks of C-TiO₂ initially shifted to lower angles but remained static after a critical doping content. Thus, at a low carbon content, carbon was doped into TiO₂ via interstitial doping. As the carbon content increased, carbon was gradually doped via lattice substitution. This was further confirmed by the XPS results, which showed that with the increasing carbon content, the peak intensity arising from the O-C bond produced by gap doping initially increased and then plateaued, while the peak intensity arising from the Ti-C bond increased gradually. The decreased Ti-O peak intensity further proved that more carbon replaced the oxygen in the lattice. The band gap of C-TiO₂ gradually decreased with increasing carbon doping content, which explained the red shift of the absorption edge. With increasing carbon content, the photocatalytic degradation efficiency of g-C₃N₄@C-TiO₂ initially increased and subsequently decreased. The g-C₃N₄@10C-TiO₂ sample exhibited the largest apparent constant of 0.036 (0.039) min⁻¹ for RhB (phenol) photodegradation. g-C₃N₄ was tightly bound to the surface of C-TiO₂ by π -conjugate and hydrogen bonding.

The novel g-C₃N₄@C-TiO₂ heterojunction exhibited a direct Z-scheme photocatalytic mechanism. Appropriate carbon doping content and surface modification of g-C₃N₄ introduced new non-local impurity levels and surface states in the catalyst, which more efficiently separated and transferred photogenerated electrons, enhancing the photocatalytic activity of the g-C₃N₄@C-TiO₂ heterostructure photocatalysts.

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Graphical Abstract

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Defect-assisted surface modification enhances the visible light photocatalytic performance of g-C₃N₄@C-TiO₂ direct Z-scheme heterojunctions

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Novel g-C₃N₄@C-TiO₂ heterojunction exhibiting a direct Z-scheme photocatalytic mechanism. Appropriate amounts of carbon doping introduced new non-local impurity levels into the catalyst, which more efficiently transferred photogenerated electrons, enhancing the photocatalytic activity.

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缺陷辅助表面修饰提高g-C₃N₄@C-TiO₂直接Z型异质结的可见光光催化性能

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摘要: 光催化技术被认为是解决能源和环境问题的最有前途方法之一。较高光催化活性的石墨相氮化碳(g-C₃N₄)及碳掺杂TiO₂(C-TiO₂)的制备及性能一直是环境光催化研究的热点, 然而, 单一光催化剂存在光生电子空穴易复合及量子效率低等问题。

本课题组曾通过简单的水辅助煅烧法成功制备了纳米多孔g-C₃N₄, 结果发现, 多孔g-C₃N₄光催化活性较体相的明显提高, 但光催化效率仍不够理想, 原因是光生电子空穴复合较严重。传统的制备C-TiO₂的方法亦存在一些不足, 如需要添加碳源或碳组分聚集体。我们采用原位掺杂的方法合成了含有一定氧空位和活性位的纳米碳改性的C-TiO₂, 后辅以简单的

化学气相沉积法构建了g-C₃N₄表面修饰的g-C₃N₄@C-TiO₂。结果表明,相比纯g-C₃N₄, TiO₂及C-TiO₂, g-C₃N₄@C-TiO₂具有更高的光催化活性;但其原因及碳掺杂态的影响尚不清楚。基于此,本文采用X射线光电子能谱技术(XPS)、透射电子显微镜(TEM)、电化学阻抗谱(EIS)、光致发光谱(PL)、电子顺磁共振技术(EPR)及理论计算等手段研究了g-C₃N₄@C-TiO₂光催化活性提高的原因和机理。

XPS结果表明,随着碳含量的增加,间隙掺杂产生的O-C键的峰值强度先增大后趋于稳定,而晶格取代掺杂产生的Ti-C键的峰值强度逐渐增大。Ti-O峰的减少进一步证明了更多的碳取代了氧晶格的位置。随着碳掺杂量的增加,C-TiO₂的带隙逐渐减小,因而吸收边红移;同时,g-C₃N₄@C-TiO₂的光催化降解效率先升高后降低。g-C₃N₄@C-TiO₂对RhB(苯酚)光降解的最大表观速率常数为0.036(0.039) min⁻¹,分别是纯TiO₂, 10C-TiO₂, g-C₃N₄和g-C₃N₄@TiO₂的150(139), 6.4(6.8), 2.3(3)和1.7(2.1)倍。g-C₃N₄通过 π -共轭和氢键与C-TiO₂表面紧密结合,在催化剂中引入了新的非局域杂质能级和表面态,可以更有效地分离和转移光生电子,因而光催化活性增加。由此可见,碳掺杂状态和g-C₃N₄原位沉积表面改性对g-C₃N₄@C-TiO₂复合光催化剂性能的影响很大。

关键词: 光催化剂; 异质结; 直接Z型; 掺杂; 修饰

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