



Enhanced photocatalytic activity of TiO₂ nanoparticles using WS₂/g-C₃N₄ hybrid as co-catalyst

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Abstract: TiO₂/WS₂/g-C₃N₄ composite photocatalysts were synthesized by a liquid-exfoliation-solvothermal method. In this process, the WS₂/g-C₃N₄ nano-sheets were prepared by liquid-exfoliation method from the bulk WS₂ and C₃N₄ in the alcohol system, and then the TiO₂ nanoparticles (NPs) grew on the WS₂/g-C₃N₄ nano-sheets by in-situ synthesized technique. The photocatalytic activity of the as-prepared samples was evaluated by photocatalytic degradation of methyl orange (MO). The results showed that the as-prepared samples exhibited higher photocatalytic activities as compared to the pure TiO₂, g-C₃N₄ and TiO₂/g-C₃N₄ composite. The enhanced photocatalytic activities of TiO₂/WS₂/g-C₃N₄ photocatalysts could be attributed to the synergistic effect of heterostructure between TiO₂ NPs and WS₂/g-C₃N₄ nano-sheets, which could efficiently improve the separation of photogenerated electron/hole pairs and utilization efficiency of photons. The quenching tests of radicals indicated that $\cdot\text{O}_2^-$ had crucial effect on degradation of MO, which demonstrated that $\cdot\text{O}_2^-$ was the main active radical in photocatalytic reaction process.

Key words: g-C₃N₄; TiO₂; WS₂; photocatalysis; liquid-exfoliation; solvothermal method

1 Introduction

TiO₂ has been extensively and deeply investigated to decompose organic pollutants in environment purification for its high photocatalytic activity, excellent chemical stability and inexpensive property. However, pure TiO₂ has low efficiency in utilization of solar energy and high recombination rate of photogenerated carriers. Currently, numerous methods have been attempted to enhance the photocatalytic activity of TiO₂. Among these methods, TiO₂ coupling with layered semiconductors, such as MoS₂, WS₂, and SnS₂, has been attracted much attention to obtain the formation of heterostructure junction and novel TiO₂-based photocatalysts with high photocatalytic activity for its simple preparation process. LENG et al [1] reported a TiO₂-pristine-graphene hybrid via a continuous supercritical solvothermal technique that facilitated the complete degradation of methyl orange under UV light for 180 min. BASSAID et al [2] reported a simple sol-gel method to fabricate WS₂/TiO₂ composite photocatalyst and achieve intimate contact between TiO₂ and WS₂, which enhanced photocatalytic activity of WS₂/TiO₂ to decompose orange II under UV light.

MIRANDA et al [3] reported a simple impregnation method to obtain g-C₃N₄/TiO₂ composite, which can efficiently promote the separation of photogenerated electron-hole pairs and improve the photocatalytic activity of TiO₂. The synergetic effect between catalysts significantly enhanced the photocatalytic performance in degrading phenol under UV irradiation.

Graphitic carbon nitride material (g-C₃N₄) has been studied a lot for the unique properties in heat endurance and chemical resistance, as well as the layered structure similar to those of graphene. It is also considered as the most stable allotrope of C-N composite for its primary building block of tri-s-triazine [4]. Since the researches about using bulk g-C₃N₄ as photocatalyst for water splitting were reported, massive efforts have been taken to study the combining bulk g-C₃N₄ with various semiconductors to obtain composite photocatalysts with excellent photocatalytic activity, such as g-C₃N₄-CdS [5,6], g-C₃N₄/Ag₃PO₄ [7], CuO@TiO₂ [8], g-C₃N₄/SnO₂ [9] and TiO₂/g-C₃N₄ [10]. The combination of TiO₂ and g-C₃N₄ has been attracted much more attention for their nontoxic resource and outstanding photocatalytic activity. FU et al [11] adopted a solid-state approach to synthesize TiO₂/g-C₃N₄ nano-composites. The heterostructure formed between g-C₃N₄ and TiO₂ could enhance the

photocatalytic activity for degradation of methyl blue. MUÑOZ-BATISTA et al [12] reported g-C₃N₄ modified TiO₂-based photocatalysts to disintegrate toluene under UV and visible light irradiation. In order to obtain photocatalysts with high separation rate of photoinduced carriers, some researchers employed nonmetal-doping and g-C₃N₄ to co-modify TiO₂. YANG et al [13] reported a N-doped TiO₂/g-C₃N₄ composite, which was synthesized by heating the mixture of hydrolysis product of TiCl₄ and C₃N₄, leading to decrease the recombination rate of photogenerated electron-hole pairs. PANY et al [14] reported a nano-composite of N, S-TiO₂/g-C₃N₄ prepared via in situ thermal induced polymerization method. The synergistic effect of crystallite size, the crystalline anatase phase, enlarged specific surface area was closely related to enhancement of visible-light absorption property and optimization of photocatalytic hydrogen evolution under visible-light irradiation.

In this study, a liquid-exfoliation-solvothermal method was employed to prepare TiO₂/WS₂/g-C₃N₄ composite photocatalyst for enhancing photocatalytic activity. In the first step, bulk g-C₃N₄ and WS₂ were treated by mixture solution of hydrochloric acid and ethanol to obtain WS₂/g-C₃N₄ composite with rough surface and uniform pore structure. Then, TiO₂ NPs grew on the surface of WS₂/g-C₃N₄ hybrid, which increased the specific surface area and achieved intimate contact among TiO₂, WS₂ and g-C₃N₄. The photocatalytic activities of as-prepared photocatalysts were evaluated using degradation of MO under simulated sunlight irradiation. The photocatalytic degradation mechanism was also tentatively analyzed.

2 Experimental

2.1 Materials

All reagents used in the experiments were analytically pure and purchased from the company without further purification. Among these, thiourea and titanium tetrachloride were obtained from Fuchen Chemical Reagent Corporation in China. Dicyandiamide, tertbutyl alcohol (TBA) and disodium ethylene diamine tetraacetate (EDTA-2Na) were purchased from Shanghai Lingfeng Chemical Reagent Corporation in China. Besides, tungsten disulfide (WS₂) and terephthalic acid (PTA) were purchased from Aladdin Reagent Corporation. Benzoquinone (BQ) was obtained from Sinopharm Chemical Reagent Corporation in China. Methyl orange (MO) was purchased from Nanhua Chemical Reagent Corporation in China.

2.2 Preparation and protonation of bulk g-C₃N₄

Bulk g-C₃N₄ was prepared by simple calcination [15] and protonation method [4]. Typically, 2.5 g thiourea and

2.5 g dicyandiamide were placed in a mortar and ground into a uniform powdered mixture. Then, the mixture was calcined at 500 °C for 1 h and further thermally treated at 550 °C for 2 h. And the bulk g-C₃N₄ was ground into powder at the room temperature. Finally, g-C₃N₄ was treated with 8% hydrochloric acid ethanol solution for 48 h to improve its dispersibility and surface activity, then washed with deionized water and anhydrous ethanol, and collected after drying at 80 °C over 3 h.

2.3 Preparation of TiO₂/WS₂/g-C₃N₄ composite photocatalysts

TiO₂/WS₂/g-C₃N₄ composite photocatalysts were prepared via a two-step solvothermal method. In the first step, 0.5 g bulk g-C₃N₄ and 0.02 g bulk WS₂ were dispersed in 18 mL mixed solution of hydrochloric acid and anhydrous ethanol under ultrasonic treatment for 1 h. The obtained dispersion liquid was transferred to a 25 mL teflon-lined stainless steel autoclave and heated at 80 °C for 10 h. After the autoclave was naturally cooled down to room temperature, the samples were separated by centrifuge, washed with anhydrous ethanol and dried at 60 °C over 3 h to obtain WS₂/g-C₃N₄ composite.

In the following step, the deposition of TiO₂ NPs on WS₂/g-C₃N₄ composite was carried out by solvothermal method similar to the previous report [16]. Firstly, 4 mL TiCl₄ ethanol solution (2 mol/L) and certain amount of WS₂/g-C₃N₄ composite were dispersed in 16 mL anhydrous ethanol under ultrasonic treatment for 1 h. Then, 5.6 mL mixed solution of sodium hexametaphosphate, ethanol and deionized water was slowly dropped into mixture to promote the hydrolysis of TiCl₄. Thirdly, the obtained TiO₂/WS₂/g-C₃N₄ precursor was transferred into a 25 mL Teflon-lined stainless steel autoclave and treated at 140 °C for 3 h. Finally, TiO₂/WS₂/g-C₃N₄ composite photocatalyst was received after being centrifugalized, washed with anhydrous ethanol and dried at 80 °C.

In order to simply signify the prepared samples, WS₂/g-C₃N₄ composite was denoted as WG. Also, TiO₂/WS₂/g-C₃N₄ composite photocatalysts were marked as TiO₂/WG-*x*, where *x* represented the mass fraction of WG composite to TiO₂ NPs and was controlled to be 3%, 5%, 7% and 9%. Besides, for comparison, TiO₂/g-C₃N₄ composite photocatalyst was also prepared via the similar two-step solvothermal process without the addition of WS₂.

2.4 Characterization

FT-IR spectra of TiO₂/WS₂/g-C₃N₄ composite photocatalyst were recorded on Bruker Tensor-27. XRD analysis was carried out to determine the crystalline structure of samples at room temperature with a Bruker D8 Advance X-diffractometer using Cu K_α radiation

($\lambda=1.5406$ Å), operated at 40 kV and 40 mA, and a scanning speed of 5 (°)/min in the 2θ range from 5° to 80°. The specific surface area was performed at the temperature of liquid nitrogen using a Beishide 3H-2000PS1 analyzer. The images of surface morphologies were taken with Merlin scanning electron microscope (SEM). The composition and chemical state of the sample were analyzed by the ULVAC-PHI PHI X-tool X-ray photoelectron spectrometer, using Al K_{α} as X-ray source. Ultraviolet-visible diffraction spectra (UV-vis DRS) were carried out on a Hitachi U-3010 spectrophotometer with wavelength range from 800 to 200 nm, using BaSO₄ as a reflectance standard. UV-vis patterns were recorded on a Shimadzu UV-2450 spectrophotometer. Photoluminescence (PL) spectra were collected on a JASCO FP-6500 type fluorescence spectrophotometer with 321 nm excitation source over a wavelength range from 300 to 800 nm. Additionally, the photocatalytic degradation of MO was carried out in a SGY-I multifunction photo-reactor apparatus (Nanjing Sidongke Co., China), using a 500 W xenon lamp as light source.

2.5 Evaluation of photocatalytic activity

Photocatalytic activity of TiO₂/WS₂/g-C₃N₄ composite photocatalysts was estimated by photocatalytic degradation of MO under the light irradiation in a photoreaction apparatus. In the experiments, a 500 W xenon lamp was employed as the light source to provide visible light. In a typical experiment, 50 mg photocatalyst was dispersed in 250 mL of 20 mg/L MO aqueous solution. Firstly, the suspension was magnetically stirred in the dark for 30 min to achieve adsorption-desorption equilibrium of MO on the surface of photocatalyst. Then, the suspension was exposed to simulated sunlight irradiation and 4 mL of sample was collected with each irradiation time interval of 10 min. After 60 min of irradiation, the collected samples were centrifugalized to remove photocatalyst and monitored using an UV-vis spectrophotometer at 464 nm with deionized water as a reference sample. The concentration of MO was directly calculated by its characteristic absorption peak at 464 nm. And the degradation rate (η) of MO under simulated sunlight was calculated by the following equation: $\eta = C_i / C_0 \times 100\%$, where C_i and C_0 are the concentrations of MO in solution at each given time and initial one.

3 Results and discussion

3.1 Characterization of TiO₂/WS₂/g-C₃N₄

X-ray diffraction patterns of TiO₂/WG photocatalysts, as well as TiO₂/g-C₃N₄, WS₂/g-C₃N₄ and pure

g-C₃N₄ samples are shown in Fig. 1. All recognizable peaks of TiO₂ corresponded to anatase TiO₂ (JCPDS card No. 21-1272) [17–19]. Consistent with the previous report [11], the g-C₃N₄ sample had two characteristic diffraction peaks at 13.1° and 27.4°, respectively. The intense reflection peak at 27.4° indicated the existence of interlayer stacking of aromatic systems, corresponding to the (002) plane diffraction. The low-angle diffraction peak at 13.1° corresponded to the (100) crystal plane of g-C₃N₄. As for WS₂/g-C₃N₄ composite, it can be observed that the characteristic diffraction peaks of WS₂ (JCPDS card No. 08-0237) and g-C₃N₄ appeared in the spectra, illustrating that g-C₃N₄ and WS₂ coexisted in the composite. Besides, the addition of WS₂/g-C₃N₄ and g-C₃N₄ decreased the average grain size of TiO₂ NPs, but had no obvious influence on the crystalline structure, suggesting that WS₂/g-C₃N₄ and g-C₃N₄ suppressed the growth of TiO₂ NPs to some extent. As shown in Table 1, the average size of TiO₂ NPs in composites was less than 10 nm, which indicated that the size of TiO₂ NPs was under control when coupled with WS₂/g-C₃N₄ hybrid.

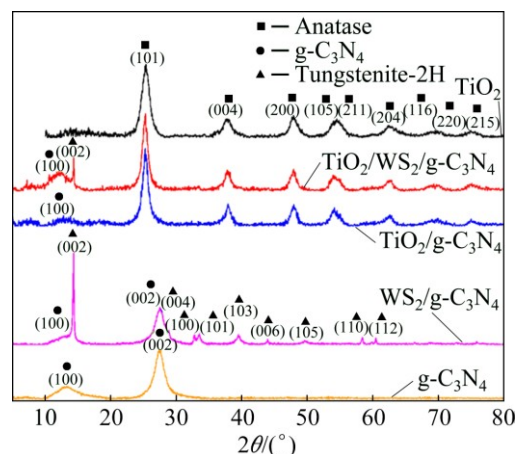


Fig. 1 XRD patterns of as-prepared TiO₂/WS₂/g-C₃N₄, TiO₂/g-C₃N₄, TiO₂, WS₂/g-C₃N₄ and g-C₃N₄

Table 1 Surface morphological properties of prepared samples

Sample	<i>D</i> /nm	<i>S</i> _{BET} /(m ² ·g ⁻¹)
TiO ₂	10.4	270.0
g-C ₃ N ₄	—	8.3
WS ₂ /g-C ₃ N ₄	—	8.8
TiO ₂ /g-C ₃ N ₄	7.1	243.0
TiO ₂ /WG-5	7.8	267.2

In order to analyze the interactions among TiO₂, WS₂ and g-C₃N₄, FT-IR spectrometer was employed to characterize TiO₂/WS₂/g-C₃N₄, TiO₂/g-C₃N₄, TiO₂, WS₂/g-C₃N₄ and g-C₃N₄, and the results are shown in Fig. 2. For the pure g-C₃N₄, three main absorption bands were observed around 3200 cm⁻¹, 1200–1700 cm⁻¹ and 808 cm⁻¹, respectively. The broad band at 3200 cm⁻¹ was

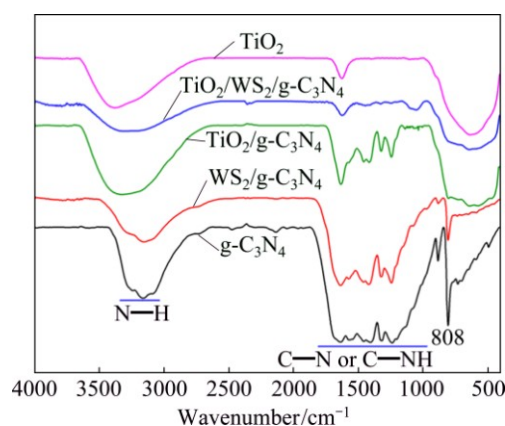


Fig. 2 FT-IR spectra of $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$, $\text{TiO}_2/\text{g-C}_3\text{N}_4$, TiO_2 , $\text{WS}_2/\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4$ samples

attributed to the stretching vibration modes of N—H and O—H groups. The intense absorption region at 1200–1700 cm^{-1} was composed of peaks at 1640, 1573, 1413, 1318 and 1240 cm^{-1} , which were associated with the stretching modes of CN heterocycles. Additionally, the peak at 808 cm^{-1} can be ascribed to out of plane bending modes of tri-s-triazine ring which has been widely accepted as the primary building block of $\text{g-C}_3\text{N}_4$ [20]. Due to the small amount of WS_2 in composite, there was no obvious difference in FT-IR spectra between $\text{WS}_2/\text{g-C}_3\text{N}_4$ composite and $\text{g-C}_3\text{N}_4$. In terms of TiO_2 , the broad peak at 400–700 cm^{-1} was characteristic of Ti—O stretching and Ti—O—Ti bridging stretching modes. And peaks observed at 3430 and 1630 cm^{-1} were attributed to the absorption of O—H stretching vibration and O—H bending mode, respectively [21]. Compared with TiO_2 , it is noted that major characteristic peaks of

TiO_2 existing in the $\text{TiO}_2/\text{WG-5}$ and $\text{TiO}_2/\text{g-C}_3\text{N}_4$ composite photocatalysts. Besides, it can be noted that there was an apparent redshift of the absorption of O—H stretching vibration at about 3300 cm^{-1} , indicating the strong interaction between TiO_2 and $\text{WS}_2/\text{g-C}_3\text{N}_4$ composite. The interaction was conducive to the intimate contact among TiO_2 , WS_2 and $\text{g-C}_3\text{N}_4$ and facilitated the separation of photogenerated electron/hole pairs.

SEM images of bulk WS_2 , bulk $\text{g-C}_3\text{N}_4$, $\text{WS}_2/\text{g-C}_3\text{N}_4$ hybrid and $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$ composite photocatalyst are shown in Fig. 3. From Figs. 3(a) and (b), it can be observed that bulk WS_2 displayed a lamellar structure with a lamellar thickness of about 200 nm while $\text{g-C}_3\text{N}_4$ showed the destruction of the surface layered structure after $\text{g-C}_3\text{N}_4$ was treated by protonation, which were consistent with the previous research [4]. In terms of $\text{WS}_2/\text{g-C}_3\text{N}_4$ composite (Fig. 3(c)), the surface morphology showed a breaking up of both laminated and stacking structure, as well as the development of pore structure among single layers. Besides, the formation of nanoparticles on the surface of the composite was in favor of the preparation of heterostructure between TiO_2 and $\text{WS}_2/\text{g-C}_3\text{N}_4$ hybrid. In $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$ photocatalyst (Fig. 3(d)), TiO_2 NPs uniformly aggregated covering $\text{WS}_2/\text{g-C}_3\text{N}_4$ composite to achieve a rough surface with large specific surface area (S_{BET}) which was beneficial to improve the absorption of degradation products (Table 1) [3].

In order to further investigate the components and chemical state of elements in $\text{TiO}_2/\text{WG-5}$ composite photocatalyst, XPS was conducted to characterize the prepared photocatalyst and the results are shown in Fig. 4. C 1s (284.5 eV) peak was referred to the standard

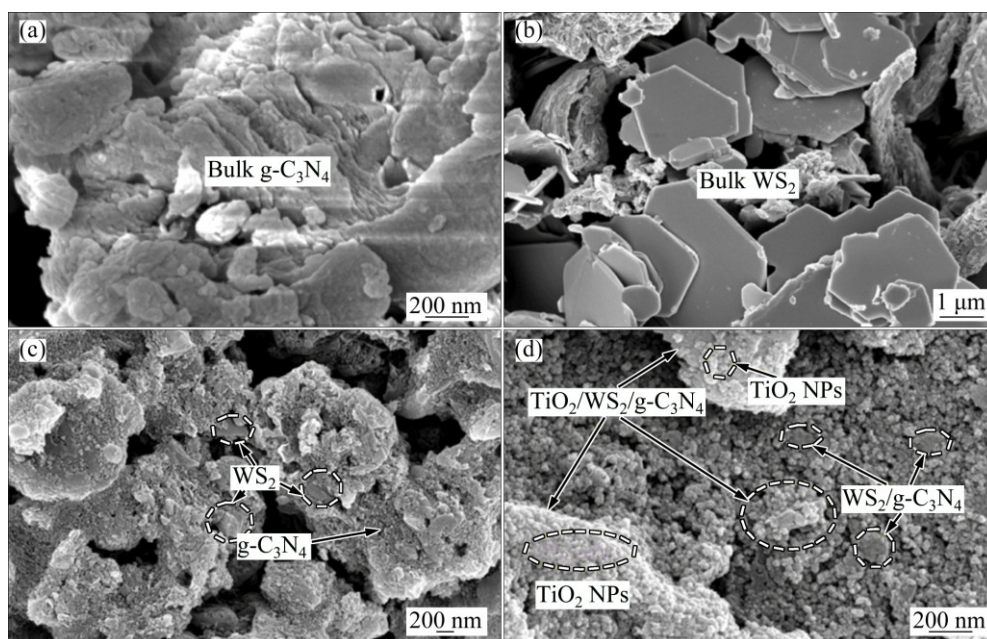


Fig. 3 SEM images of bulk $\text{g-C}_3\text{N}_4$ (a), bulk WS_2 (b), $\text{WS}_2/\text{g-C}_3\text{N}_4$ hybrid (c), and $\text{TiO}_2/\text{WG-5}$ composite photocatalyst (d)

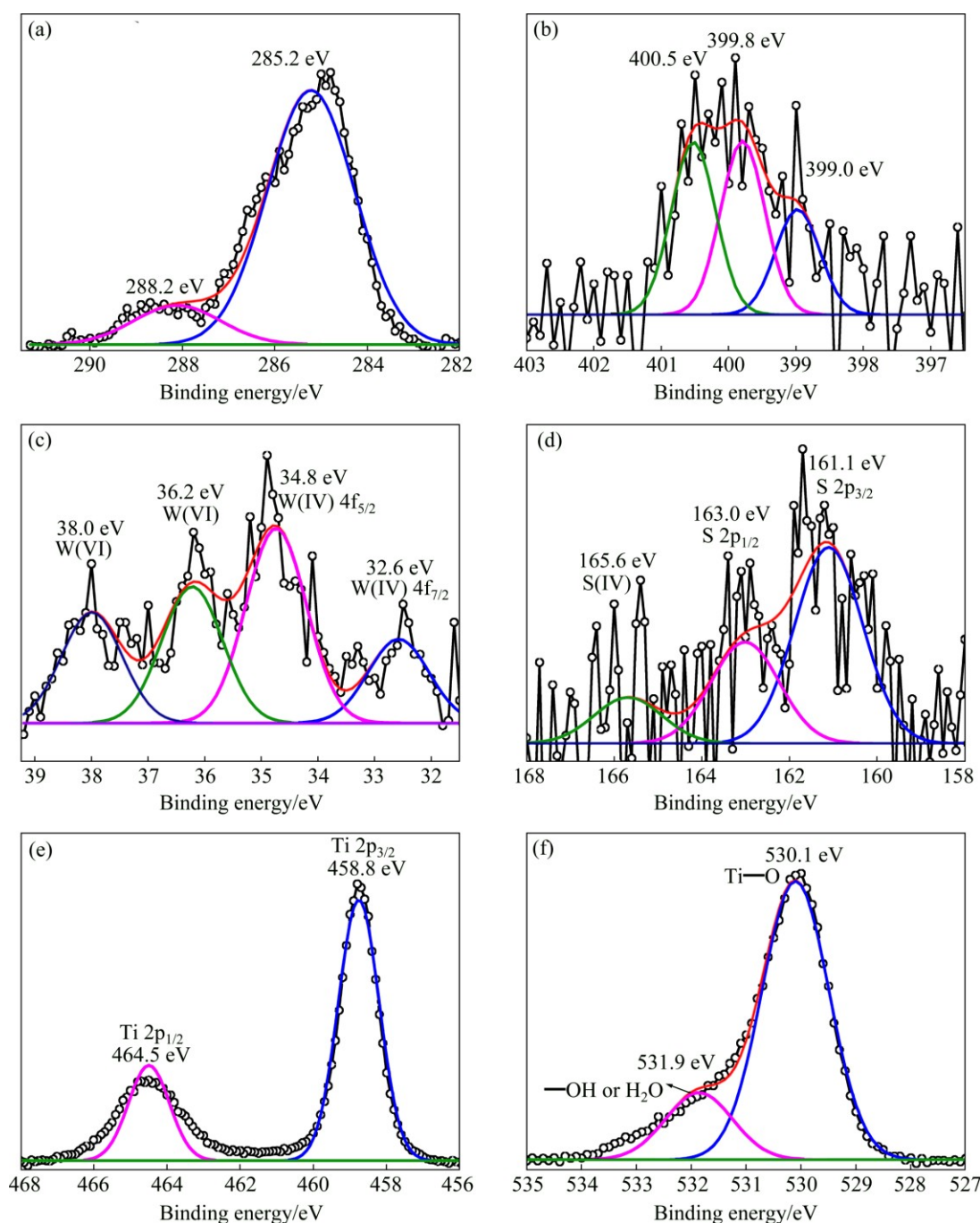


Fig. 4 XPS spectra of $\text{TiO}_2/\text{WG-5}$ composite photocatalyst: (a) C 1s; (b) N 1s; (c) W 4f; (d) S 2p; (e) Ti 2p; (f) O 1s

of all binding energies in XPS analysis. Two XPS signals can be observed at the binding energies of 285.2 and 288.2 eV (Fig. 4(a)), which were assigned to defect-containing sp^2 -hybridized carbon atoms present in graphitic domains and sp^3 -bonded C of $\text{N}-\text{C}=\text{N}_2$, respectively [22]. The peak of N 1s was decomposed into three peaks at 399.0, 399.8 and 400.5 eV (Fig. 4(b)), which were ascribed to the groups of N ($\text{C}=\text{N}-\text{C}$), ($\text{N}-(\text{C})_3$ and $\text{C}-\text{N}-\text{H}$), respectively [3,23]. From Fig. 4(c), the peaks at the binding energies of 32.6 and 34.8 eV were observed, which were assigned to $\text{W } 4\text{f}_{7/2}$ and $\text{W } 4\text{f}_{5/2}$ of W^{4+} , respectively [24]. The binding

energies of 36.2 and 38.0 eV were ascribed to the peak of W^{6+} , which was attributed to the oxidation of WS_2 [25,26]. As shown in Fig. 4(d), the S 2p binding energies at 161.1 and 163.0 eV were observed, which indicated that the S^{2-} existed in the composite photocatalyst [24]. It can be observed two XPS signals at the binding energies of 458.8 eV and 464.5 eV in Fig. 4(e), indicating the existence of Ti^{4+} in photocatalyst [27]. The O1s peaks were identified at around 530.1 and 531.9 eV in Fig. 4(f), which were attributed to the $\text{Ti}-\text{O}$ in TiO_2 and $\text{H}-\text{OH}$ groups, respectively [28]. These results demonstrated that the prepared $\text{TiO}_2/\text{WS}_2/\text{g}-\text{C}_3\text{N}_4$ composite did not

transform to other materials except a small amount of WS_2 dissolved by hydrochloric acid solution.

3.2 Photocatalytic performance of $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$

UV-vis diffuse reflection spectra of as-prepared $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and $\text{TiO}_2/\text{WG-5}$ composite photocatalysts, as well as TiO_2 , $\text{g-C}_3\text{N}_4$ and $\text{WS}_2/\text{g-C}_3\text{N}_4$ composite are shown in Fig. 5. It can be observed that $\text{g-C}_3\text{N}_4$ exhibited intense optical absorption in the region of wavelength less than 450 nm while had little absorption in the region of wavelength more than 450 nm, which was attributed to its narrow band gap of 2.7 eV [5]. Bulk WS_2 had excellent absorption capacity in ultraviolet and visible light region for its indirect band gap of around 1.4 eV and a direct band gap of 2.01 eV [29], as well as 1.72 eV of nano WS_2 [2]. Accordingly, $\text{WS}_2/\text{g-C}_3\text{N}_4$ composite achieved stronger visible-light absorption than pure $\text{g-C}_3\text{N}_4$. Afterwards, compared with pure TiO_2 , $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$ photocatalyst had stronger absorption in visible-light region with its absorption band edge red shift. Therefore, the results indicated that the prepared $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$ composite photocatalyst had excellent optical absorption in the ultraviolet and visible regions.

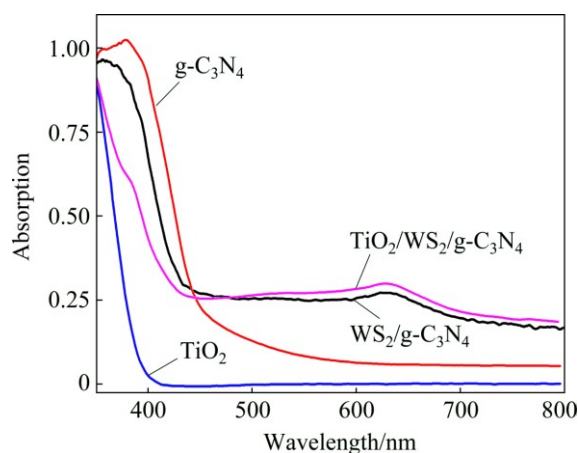


Fig. 5 UV-vis diffuse reflection spectra of TiO_2 , $\text{g-C}_3\text{N}_4$, $\text{WS}_2/\text{g-C}_3\text{N}_4$ composite and $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$ composite photocatalysts

The photocatalytic activity of the prepared samples was evaluated by degradation of MO under simulated sunlight irradiation and the results are shown in Fig. 6. In the absence of photocatalyst, there was no noticeable curve descending of C_t/C_0 in MO solution, ruling out the direct photodegradation of MO under illumination. For comparison, pure TiO_2 was conducted to photocatalytic degradation of MO under the same conditions, showing lower photocatalytic activity. Because the heterostructure junction was produced between TiO_2 NPs and bulk $\text{g-C}_3\text{N}_4$ [11,12,30], $\text{TiO}_2/\text{g-C}_3\text{N}_4$ photocatalyst achieved enhanced the photocatalytic performance. As for the

prepared $\text{TiO}_2/\text{WG-}x$ ($x=3, 5, 7$ and 9 , respectively) composite photocatalysts, all of them exhibited excellent photocatalytic degradation with MO degradation rate of 84.7%, 95.8%, 94.8% and 81.2% under simulated-sunlight irradiation for 60 min, respectively. And the optimum mass ratio of WG to TiO_2 was 0.05:1, which showed the best photocatalytic behavior. Additionally, the physical mixtures of TiO_2-WS_2 and $\text{TiO}_2-\text{g-C}_3\text{N}_4$ were prepared by blending $\text{TiO}_2/\text{WS}_2-0.2$ and $\text{TiO}_2/\text{g-C}_3\text{N}_4-4.8$ according to the mass ratio of 1:24. The photocatalytic performance of the prepared mixture was obviously inferior to that of TiO_2/WG composite photocatalysts, illustrating that a unique heterostructure was formed among TiO_2 NPs, bulk WS_2 and bulk $\text{g-C}_3\text{N}_4$. In other words, the synergistic effect of bulk WS_2 and $\text{g-C}_3\text{N}_4$ promoted the separation of photogenerated hole-electron pairs in TiO_2/WG composite photocatalysts and improved their photocatalytic activity [31].

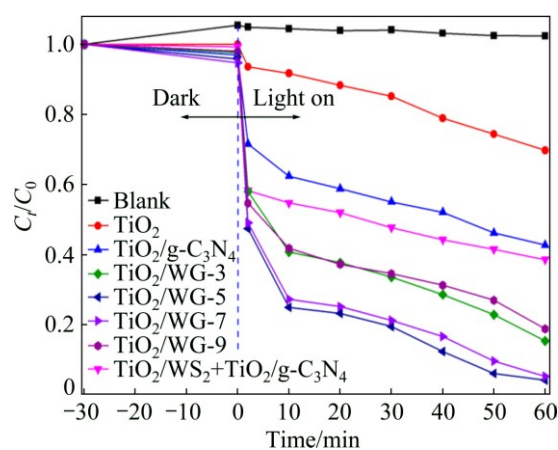


Fig. 6 Photocatalytic activities of TiO_2 , $\text{TiO}_2/\text{g-C}_3\text{N}_4$, $\text{TiO}_2/\text{WS}_2+\text{TiO}_2/\text{g-C}_3\text{N}_4$ and $\text{TiO}_2/\text{WG-}x$ ($x=3, 5, 7$ and 9) photocatalysts for MO degradation under simulated sunlight

3.3 Photocatalytic mechanism of $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$

Fluorescence technique was an important method to evaluate the migration, transfer and recombination of photogenerated hole/electron pairs in photocatalysts [5]. Figure 7 showed the fluorescence spectra of pure TiO_2 , $\text{WS}_2/\text{g-C}_3\text{N}_4$, $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$ samples with excitation wavelength of 321 nm. It can be observed that pure $\text{g-C}_3\text{N}_4$ had a strong fluorescence emission peak at about 441 nm due to its high recombination rate of photoinduced holes and electrons. In terms of $\text{WS}_2/\text{g-C}_3\text{N}_4$, $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$ photocatalysts, the PL intensities significantly decreased due to the hetero-structures, reducing the recombination of photoexcited electron/hole pairs. Moreover, 398 nm was the quenching of intrinsic fluorescence of TiO_2 , and the PL intensities of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and ternary $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$ composites

at 398 nm are lower than that of pure TiO_2 , suggesting a lower recombination of photo-generated e/h^+ pairs [32].

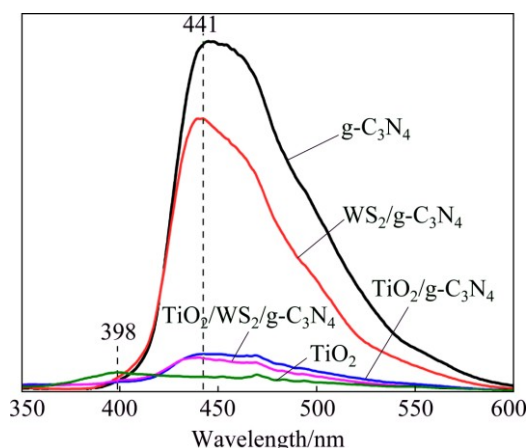


Fig. 7 PL spectra of pure TiO_2 , $\text{WS}_2/\text{g-C}_3\text{N}_4$, $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$ samples

During the photocatalytic degradation process, it was known that main reactive species were generated to oxidize organic pollutants [33,34]. To elucidate the photocatalytic reaction mechanism of TiO_2/WG photocatalyst, TBA, EDTA-2Na and BQ were considered as scavengers of hydroxyl radicals ($\cdot\text{OH}$), holes (h^+) and superoxide radical ions ($\cdot\text{O}_2^-$) [35], respectively. Figure 8 showed that the photocatalytic degradation efficiency of MO decreased significantly in the presence of TBA and BQ compared with that of TiO_2/WG photocatalytic degradation system without addition of capture agent. On the other hand, the appearance of EDTA-2Na in photocatalysts system promoted the photocatalytic degradation of MO. Therefore, it was concluded that $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ played an important role in the photocatalytic degradation of MO while h^+ recombining with e^- led to low efficiency in photocatalytic degradation of MO.

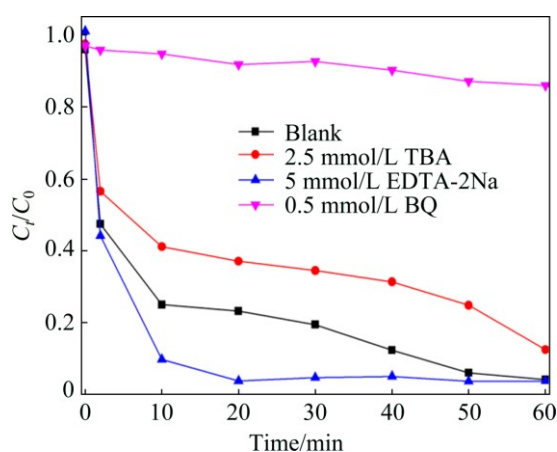


Fig. 8 Photocatalytic degradation of MO over TiO_2/WG -5 in the presence of TBA, EDTA-2Na and BQ as capture agent

To further investigate the photocatalytic reaction mechanism, hydroxyl radicals ($\cdot\text{OH}$) were detected in the TiO_2/WG -5 photocatalytic system under simulated sunlight irradiation by fluorescence technique. Terephthalic acid (PTA) was employed as probe molecule to react with hydroxyl radicals on the surface of photocatalyst and produce hydroxyl terephthalic acid (PTAOH). Figure 9 showed that the fluorescence spectra excited at 321 nm in the TiO_2/WG -5 photocatalyst system with the addition of different capture agents. Compared with TiO_2/WG -5 photocatalytic system without addition of capture agents, the presence of TBA could slightly reduce the fluorescence intensity of hydroxyl radicals while BQ suppressed the formation of hydroxyl radicals severely. According to the entrapping experimental, removing the h^+ could obviously enhance the photocatalytic activity of composite photocatalyst, thus, the PTA could be degraded by the photocatalyst when adding the EDTA-2Na into the reaction system, leading to the decrease of PL intensity.

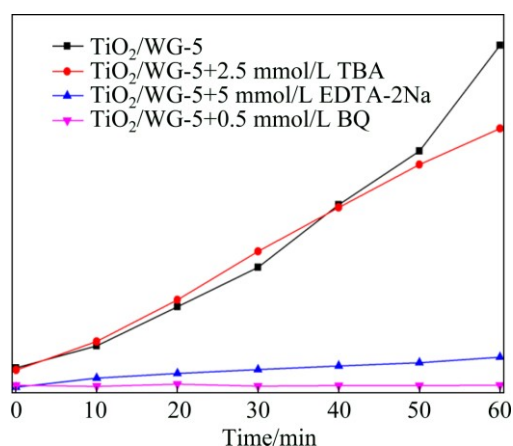


Fig. 9 Fluorescence intensity at 450 nm against irradiation time in TiO_2/WG -5 photocatalyst system with different capture agents

According to the results of carrier trapping experiments and fluorescence spectra, the $\cdot\text{OH}$ was mainly produced by the transform of $\cdot\text{O}_2^-$. It was universally accepted that hydroxyl radicals ($\cdot\text{OH}$) in photocatalytic system were mainly generated by following processes (Eqs. (1) and (2)): reactive electrons reduced oxygen absorbed on the surface of photocatalyst to superoxide radical ions ($\cdot\text{O}_2^-$), then the formed $\cdot\text{O}_2^-$ combined with an electron to finally produce $\cdot\text{OH}$ [33,35]. Meanwhile, $\text{g-C}_3\text{N}_4$, as well as TiO_2 exhibited adequate reduction potential to achieve the formation of $\cdot\text{OH}$ via a two-electron reduction reaction process [36]. At the same time, EDTA-2Na reacting with h^+ improved the separation rate of photoinduced carriers and promoted the photocatalytic degradation of MO. The

separated electrons reduced oxygen to $\cdot\text{O}_2^-$ and then the formed $\cdot\text{O}_2^-$ degraded MO under irradiation, which corresponded to the results of carrier trapping experiments. Therefore, we can draw a conclusion from the analysis above. $\cdot\text{O}_2^-$ intermediate species mainly took the responsibility to degrade the MO while $\cdot\text{OH}$ played the minor role in degradation of MO in photocatalytic system under simulated sunlight.



A probable reaction mechanism of photocatalytic degradation of MO was proposed in Fig. 10. When the photocatalytic system of $\text{TiO}_2/\text{WG-5}$ was exposed to the illumination, the electrons on the valence band of TiO_2 , $\text{g-C}_3\text{N}_4$ and WS_2 were excited to their conduction bands and generated electron-hole pairs (Eq. (3)). On one hand, because the position of conduction band of $\text{g-C}_3\text{N}_4$ and WS_2 were lower than that of TiO_2 , photoexcited electrons were transformed from conduction band of $\text{g-C}_3\text{N}_4$ and WS_2 to that of TiO_2 simultaneously. The h^+ on the valence band of $\text{g-C}_3\text{N}_4$ and WS_2 cannot oxidize H_2O into $\cdot\text{OH}$ owing to the lower oxidation potential. Moreover, the aggregated electrons on the conduction band of TiO_2 moved to the surface of photocatalyst and reduced absorbed O_2 to $\cdot\text{O}_2^-$ (Eq. (4)). Certain amount of $\cdot\text{O}_2^-$ further reacted with electrons to form $\cdot\text{OH}$ (Eq. (5)). On the other hand, some of photoinduced holes in the valence band of TiO_2 directly oxidized H_2O to $\cdot\text{OH}$ while others injected into that of $\text{g-C}_3\text{N}_4$ and WS_2 as a result of electric potential of valence band of TiO_2 superior to others. Finally, these formed active species ($\cdot\text{O}_2^-$, $\cdot\text{OH}$) completely degraded MO under irradiation (Eq. (6)). Thus, the synergetic effect of $\text{g-C}_3\text{N}_4$ and WS_2 , enlargement of the specific surface area and high separation of photoinduced carriers, significantly improved the photocatalytic activity of as-prepared photocatalysts.

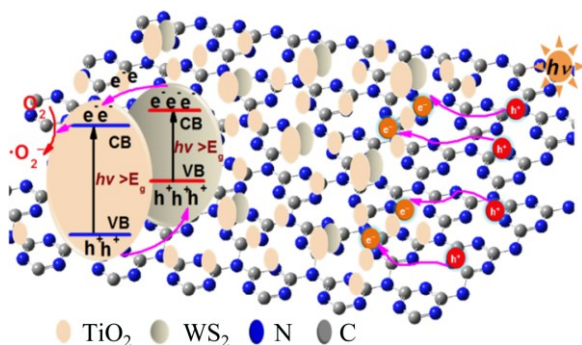
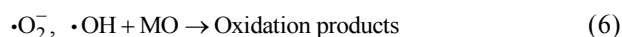
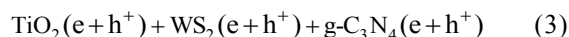
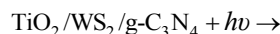


Fig. 10 Photocatalytic mechanism for MO degradation in TiO_2/WG photocatalytic system under simulated sunlight



4 Conclusions

$\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$ composite photocatalysts were successfully synthesized by a two-step solvothermal treatment method. In the first step, solvothermal treatment, $\text{WS}_2/\text{g-C}_3\text{N}_4$ composite was prepared with rough surface and uniform pore structure. In the following process, the prepared $\text{WS}_2/\text{g-C}_3\text{N}_4$ composite was successfully coated by TiO_2 nanoparticle, which achieved the intimate contact among TiO_2 , bulk WS_2 and $\text{g-C}_3\text{N}_4$. The characterization results indicated that as-prepared photocatalysts had good optical absorption property in ultraviolet and visible light regions and low recombination rate of photogenerated electron-hole pairs compared with pure TiO_2 and $\text{TiO}_2/\text{g-C}_3\text{N}_4$ photocatalysts. Moreover, $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$ composite photocatalysts exhibited excellent photocatalytic activity for degradation of MO with degradation rate of more than 95% under irradiation for 60 min. The results of carrier trapping experiments and fluorescence spectra illustrated that $\cdot\text{O}_2^-$ rather than $\cdot\text{OH}$ and h^+ played the key role in photocatalytic degradation of MO.

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以 $\text{WS}_2/\text{g-C}_3\text{N}_4$ 杂化复合物为共催化剂 提高 TiO_2 光催化活性

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摘 要: 采用液相剥离和溶剂热法制备 $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$ 复合光催化剂。通过液相剥离的方法在乙醇体系中将块状 WS_2 和 C_3N_4 剥离得到相应的纳米片; 利用热处理法使 TiO_2 纳米粒子原位生长并固定于 $\text{WS}_2/\text{g-C}_3\text{N}_4$ 纳米片上。采用光催化降解甲基橙(MO)来评价 $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$ 的光催化活性。结果表明, $\text{TiO}_2/\text{WS}_2/\text{g-C}_3\text{N}_4$ 复合光催化剂的光催化活性远高于纯态 TiO_2 , $\text{g-C}_3\text{N}_4$ 及 $\text{TiO}_2/\text{g-C}_3\text{N}_4$ 复合物, 这主要归因于 $\text{WS}_2/\text{g-C}_3\text{N}_4$ 杂化复合物与 TiO_2 纳米粒子之间的协同作用, 有效促进了复合光催化剂中光生电子/空穴对的分离, 提高了光子的利用率。活性自由基的捕获实验表明, $\cdot\text{O}_2^-$ 对 MO 的降解起着决定性的作用, 这说明 $\cdot\text{O}_2^-$ 是光催化反应过程中主要的活性自由基。

关键词: $\text{g-C}_3\text{N}_4$; TiO_2 ; WS_2 ; 光催化; 液相剥离; 溶剂热法

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